



## Oxygen reduction reaction on electrochemically deposited silver nanoparticles from non-aqueous solution

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### ARTICLE INFO

#### Keywords:

Electrodeposition  
Ag nanoparticles  
Silver catalyst  
Oxygen reduction  
Electrocatalysis

### ABSTRACT

Silver was electrodeposited onto glassy carbon electrode from 0.1 mM AgClO<sub>4</sub> acetonitrile solution containing 0.1 M LiClO<sub>4</sub>. The electrochemical deposition was carried out at constant potential of  $-0.5$  V vs. SCE. The surface morphology was studied by scanning electron microscopy and the average particle size was determined to be 45 nm to 90 nm when increasing the deposition time from 10 s to 300 s. The rotating disk electrode (RDE) method was employed for oxygen reduction studies in 0.1 M KOH solution. It was determined that the final product for the reaction is water and the rate-determining step is the slow transfer of the first electron to O<sub>2</sub> molecule. The specific activities (SA) and mass activities (MA) were calculated from the RDE results and the latter was independent of the deposition time. The method used to determine electroactive surface area of Ag influenced substantially the determination of SA values.

### 1. Introduction

The oxygen reduction reaction (ORR) is the performance limiting reaction in low-temperature fuel cells and the best electrocatalysts for ORR are platinum-based materials [1]. Due to the high cost of Pt cheaper alternatives are sought for [2,3]. Silver is a promising catalyst material for ORR in alkaline media [3,4]. Chatenet et al. demonstrated that on Pt and Ag, both bulk polycrystalline and highly dispersed on carbon, catalyse the ORR to form water and the kinetics are in the first order towards oxygen concentration in solution [5]. The ORR activity on Ag is slightly lower than on Pt but the price of the metals makes Ag essentially more favourable [6].

Most often the discussion of the ORR performance on Ag-based catalysts is concentrated on the number of electrons transferred per O<sub>2</sub> molecule ( $n$ ). Blizanac et al. studied the ORR on low-index Ag single-crystal surfaces [7]. It was determined that the ORR on Ag is a structure sensitive reaction and the kinetics of the ORR increases in the order of Ag(100)  $\leq$  Ag(111)  $<$  Ag(110). They suggested that the structure sensitivity may arise from potential-dependent adsorption of spectator hydroxyl ions or due to variations in activation energies. It was suggested that serial 4-electron pathway occurs most likely on Ag( $hkl$ ) in KOH. However, Wang et al. suggested that the Ag nanodecahedra enclosed by (111) facet catalyse the ORR via one-step four-electron reaction pathway [8]. To elaborate the differences in the ORR activity

they modelled the system and concluded that the weaker adsorption of OH on Ag(111) facet provides higher number of active sites and thus leading to higher ORR activity on nanodecahedra as compared to nanocubes enclosed by Ag(100). When electrochemical deposition is carried out in the presence of poly(vinyl pyrrolidone) then it inhibits the crystalline growth in the [111] direction and thus yielding particles with essentially only (111) facets [9]. The ORR on those formed Ag nanosheet arrays proceeds to form water. Similar Ag nanoplatelets have been obtained when using sodium citrate as capping agent [10].

The Ag particle size may affect the value of  $n$ , as the ORR on 174 nm particles showed higher electron transfer number than 4.1 nm Ag particles [11]. However this might be similar to the findings by Neumann et al. who reported that the yield of water decreases with increasing the interdistance of particles [12]. In addition, when investigating the ORR on carbon-supported Ag nanoparticles it was found that the peroxide yield in solution phase with 10 wt% Ag/C was up to 10%, while for Ag/C catalyst with 20 wt% and higher Ag content the ring currents suggested negligible H<sub>2</sub>O<sub>2</sub> production [13]. Garcia et al. calculated that 2.7 electrons are transferred to O<sub>2</sub> molecule on 10 wt% Ag/C and thus they suggested that oxygen is also partially reduced on carbon support [14]. 20 wt% Ag/C has been suggested to be the best loading in terms of current density and mass activity [15]. In that study the tolerance of methanol was also evaluated and it was concluded that Ag/C is less affected to methanol than Pt/C catalyst. Graphene-supported silver

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nanoparticles have been shown to catalyse the ORR via series  $2e^- + 2e^-$  partway [16]. It has been suggested that the reduction of  $O_2$  on Ag/C and nitrogen-doped graphene-supported Ag proceeds via mixed two- and four-electron pathways [17–20]. In addition, Ag is a good catalyst for peroxide reduction [21]. These results clearly demonstrate that the amount of Ag on the electrode is crucial for 4-electron reduction of oxygen and it is most likely that the ORR on silver proceeds mainly via series  $2e^- + 2e^-$  transfer pathway. The particle size effect on kinetic current has been reported in numerous studies. It has been shown that smaller particles have higher electrocatalytic activity than larger ones [22–24], also opposite has been suggested [11,25] and also a peak activity at certain particle size has been reported [26]. Using Ag nanocubes it has been shown that the specific activity decreases with increasing the particle size from 12 to 38 nm [22]. However the effect described in those publications might be related to the amount of Ag, not to the particle size effect. Ohyama et al. suggested that the specific activity is not influenced by the particles larger than 10 nm and smaller than 3 nm particles might exhibit a particle size effect due to the large number of unsaturated Ag atoms and quantum dot effect [27].

The ligands used in the synthesis may also alter the ORR kinetics and mechanistic pathways, for example poly(vinyl pyrrolidone) is often used in the synthesis and it decreases the oxygen reduction current density and also the number of electrons transferred [28]. Previously we have prepared Ag nanoparticle coated multi-walled carbon nanotubes by magnetron sputtering meaning that no additional chemicals were used in the electrocatalysts preparation [29]. It was found that the  $n$  value was close to four over the entire range of potentials studied. We have prepared stabilizer-free Ag nanoparticles by plasma jet treatment and also in this case  $n$  was close to four [30]. Electrodeposition is another possible method in which stabilizers may be omitted. Ag has been electrochemically deposited onto manganese oxide-modified graphene electrode and the ORR results were promising to use such composite catalyst in alkaline fuel cell [31]. Tiwari and Nagaiah deposited Ag from aqueous solution using double voltage pulses [32]. They reported that changing the nucleation and growth potentials will result in varied morphologies of Ag. Often rather large particles ( $> 100$  nm) have been obtained [9,33–35]. The larger particles decrease the mass activities and thus procedures for the deposition of smaller Ag particles are needed. Suryanto et al. deposited Ag from protonic ionic liquids, however at best they managed to get particles with typical size from 100 to 250 nm [36].

Previously we have studied the ORR kinetics on electrochemically deposited Ag particles from aqueous path [37]. To our knowledge the ORR on Ag-based catalysts electrodeposited from acetonitrile solution has not been explored previously. In this work we have electrodeposited Ag from non-aqueous solution at constant potential regime and investigated the ORR activity on those Ag coated glassy carbon electrodes in alkaline electrolyte.

## 2. Experimental

Glassy carbon (GC) electrodes were prepared by mounting GC disks ( $d = 5$  mm, GC-20SS, Tokai Carbon) into Teflon holders. Prior to Ag deposition the GC electrodes were polished to mirror finish with 1 and  $0.3 \mu\text{m}$   $Al_2O_3$  slurries (Buehler). The polishing residues were removed by treating the electrodes in an ultrasonic bath in isopropanol and in Milli-Q water for 5 min. Bulk polycrystalline Ag ( $d = 5$  mm, 99.95%, Alfa Aesar) was used as a comparison.

The electrochemical measurements were carried out in a three-electrode glass cell. Saturated calomel electrode (SCE) was used as a reference electrode, which was separated from the working solution by Luggin capillary and all the potentials in this study are given with respect to the SCE. Pt wire separated through glass frit served as a counter electrode. The potential was applied by Autolab PGSTAT30 potentiostat/galvanostat (Metrohm Autolab B.V., The Netherlands), EDI101

rotator with CVT101 speed control unit (Radiometer, Copenhagen) were used for rotating disk electrode (RDE) experiments.

The electrochemical deposition of silver was carried out from Ar-saturated (99.999%, AGA) 0.1 mM  $AgClO_4$  in acetonitrile containing 0.1 M  $LiClO_4$  (99.8%, water-free, Sigma-Aldrich) as base electrolyte. The deposition was performed at a constant potential of  $-0.5$  V vs. SCE for up to 300 s. In what follows the electrodeposited Ag electrodes are designated as  $Ag_x$ , where  $x$  marks the deposition time in seconds. The oxygen reduction measurements were carried out in  $O_2$ -saturated (99.999%, AGA) 0.1 M KOH. The solution was prepared from KOH pellets (puriss p.a., Sigma-Aldrich) and Milli-Q water. Pb underpotential deposition experiments were conducted in 0.1 M KOH solution containing 0.5 mM  $Pb(NO_3)_2$ . The Ag was finally electrochemically stripped from the GC in Ar-saturated 0.1 M  $NaClO_4$  (Merck) by applying potential scan rate ( $\nu$ ) of  $50$  mV  $s^{-1}$ .

The surface morphology of electrodeposited Ag coatings was studied by scanning electron microscopy (SEM) employing Helios™ NanoLab 600 (FEI) instrument. The SEM sample was prepared using GC disks.

## 3. Results and discussion

### 3.1. Surface morphology

Fig. 1 displays SEM images of Ag nanoparticles deposited onto GC surface for 10, 60, 180 and 300 s. After 0.1 s the surface is almost completely empty and only some Ag particles were observed. It can be observed that the size of the particles grow and the number density increases with increasing the deposition time. After 10 s the Ag particles are approximately 45 nm in diameter, after 60 s the particles have grown to about 55 nm, 180 s yields 75 nm particles and after 300 s they are about 90 nm. Also smaller particles can be observed from the SEM images revealing that there are sufficient amount of surface sites on GC for the deposition of Ag. With shorter deposition time mostly individual particles are observed and with increased deposition time the particles start merge together as the particles grow and the surface coverage increases.

### 3.2. Cyclic voltammetry

For electrochemical characterisation the electrodeposited Ag electrodes were subjected to potential cycling in the potential range between  $-1.3$  and  $0.4$  V. A comparison of cyclic voltammetry results is presented in Fig. 2 and it can be observed that there are no characteristic peaks in the potential window from  $-1.3$  to  $-0.1$  V. The oxidation of silver starts at about  $0.1$  V and two characteristic peaks are observed. A small peak at  $0.16$  V corresponds to both dissolution of Ag and the formation of a monolayer of  $Ag_2O$ . However the origin of this peak has been considered to be complex and there have been several propositions for the origin of this peak [38]. The large peak at  $0.32$  V consists of two peaks, which have been associated with the formation of bulk phases of  $AgOH$  and  $Ag_2O$  [13,38,39]. The reduction of Ag oxides takes place at cathodic scan at about  $0.05$  V. In the literature the oxide reduction peak has been used to calculate the electroactive surface area of Ag [39,40]. However as both  $Ag_2O$  and  $AgOH$  are formed during the silver oxidation then this approach may not be reliable.

### 3.3. ORR studies

The oxygen reduction studies were carried out in  $O_2$ -saturated 0.1 M KOH solution. Fig. 3a displays a set of RDE polarisation curves for the  $O_2$  reduction reaction on electrodeposited  $Ag_{180}$ . The background current measured in  $O_2$ -free solution has been subtracted from the RDE data and only positive-going scans are displayed and were subjected for further analysis. It can be seen that the polarisation curves have a minimum at about  $-0.9$  V. When comparing the Ag coated electrodes

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