

Full Length Article

One-pot electrodeposition of cobalt flower-decorated silver nanotrees for oxygen reduction reaction

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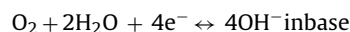
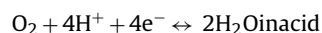
ABSTRACT

In this paper, we demonstrate a simple fabrication of bimetallic silver (Ag) and cobalt (Co) nanostructures (AgCo) with various Ag to Co relative contents via electrochemical co-deposition. A series of AgCo catalysts was electrodeposited on glassy carbon (GC) electrodes at -0.57 V vs. SCE in the deposition solutions, containing Ag precursor, Co precursor, Triton X-100, and 0.3 M KNO_3 aqueous solution, with various Ag to Co precursor concentration ratios ($1:x$, x varied from 3 to 11). The films, deposited with the total deposition charge of 0.042 C, were denoted as Ag_1Co_x . SEM and TEM analyses showed that Ag_1Co_x formed a structure consisted of flower-like Co grown on tree-like Ag backbones while it had more Co flowers with a greater x . The ORR activities were examined in 0.1 M NaOH solution with rotating disk electrode (RDE) voltammetry and Ag_1Co_7 showed the best catalytic activity. The co-deposition mechanism was further investigated by varying the deposition time of Ag_1Co_7 . At the early stage of deposition, Ag-tree branches were formed predominantly, followed by the growth of flower-like Co nanostructures on the Ag nanotrees: More Co flowers were produced on Ag backbones with longer deposition time, being attributed to both a less negative reduction potential of Ag^+ to Ag than Co^{2+} to Co and promoted Co^{2+} reduction on the initially formed Ag surface. Ag_1Co_7 electrodeposited for 200 s, consisted of $\sim 14\%$ Co, showed the greatest ORR catalytic activity which was better or comparable to noble metal Pt.

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1. Introduction

Efficient catalyst systems for oxygen reduction reaction (ORR) have been studied extensively for the development of economical and high-performance polymer electrolyte membrane fuel cells (PEMFC). ORR takes place as below [1].



There are two reaction pathways: 4-electron transfer pathway and 2,2-electron transfer pathway. The former one directly reduces O_2 to H_2O or OH^- as the final products by transferring 4 electrons while the latter one produces intermediates, H_2O_2 or HO_2^- , through 2-electron transfer before forming the final products. It has been well-known that an efficient catalyst is required to pro-

ceed ORR mostly via 4-electron transfer pathway. However, more detailed reaction mechanism is still unclear due to its complexity (i.e., O–O bond cleavage, multi-electron transfers) [2]. Although there have been some controversial mechanisms proposed, one of the plausible mechanisms is the 4-electron reduction with an initial dissociative chemisorption of O_2 [3]. According to this mechanism, oxygen atoms generated by breaking the O–O bond of O_2 are adsorbed on metal surfaces, and then reduced to H_2O or OH^- through 4-electron transfer. It implies that a superior ORR catalyst needs to be good at both cleaving the O–O bond and reducing oxygen atoms.

Silver (Ag) is one of the promising ORR catalysts for the replacement of expensive and rare platinum (Pt) owing to its decent ability of reducing oxygen atoms [2–8]. The superior electrochemical stability of Ag in basic media is also proved by the Pourbaix diagram [9]. Furthermore, the use of Ag-based catalysts makes the development of economical fuel cells feasible due to the relatively low price [10]. However, the ORR activity of Ag is still lower than that of Pt [2]. Both Pt and Ag have the same ORR rate determining step which is the initial reduction step of adsorbed oxygen atoms to form another adsorbed oxygen-containing species through one electron transfer [11–14]. According to density functional theory (DFT) calculation,

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this step at Ag requires a higher overpotential than at Pt since an Ag adsorbs oxygen atom less strongly than Pt [15]. This is a major cause of the lower ORR activity of Ag compared to Pt [16–19]. Fortunately, the bimetallic catalyst based on Ag mixed with 3d transition metals, in particular with cobalt (Co), adsorbs oxygen-containing species more strongly than pure Ag because Co has a strong binding affinity to oxygen and plays a critical role in O–O bond cleavage [3,4]. In order to be an efficient ORR catalyst, the desorption step of the reduction product is as important as the reactant adsorption step is. Another beneficial aspect of bimetallic Ag and Co catalyst (AgCo) is the moderate affinity of the reduction product to the catalyst surface which makes the product desorption properly favorable [15]. Indeed, AgCo possibly attains an optimum adsorption/desorption strength of oxygen-containing species during ORR via blending the weak and strong binding affinities of Ag and Co, respectively.

Therefore, the relative ratio between Ag and Co in an AgCo catalyst is considered to be a critical factor determining its ORR activity. Most previous studies reported that 20–30% of Co content in AgCo bimetallic catalysts had the greatest ORR activities. Fernández et al. investigated ORR currents of a series of AgCo arrays with different Ag and Co content ratios with scanning electrochemical microscopy and showed the best activity at a catalyst with Ag:Co ratio of 80:20 [3]. Loglio et al. fabricated Co monolayer islands on Ag and found that ca. 25% of Co (75:25 of Ag:Co ratio) showed the superior ORR activity [20]. Zafferoni et al. also proved that the most enhanced ORR activity was observed when ca. 33% of Co was contained within the electroplated Co on Ag microparticles [21]. According to a theoretical result, 25% of Co content in AgCo was reported to give the maximum synergic effect in terms of the Gibbs free energy [4].

AgCo bimetallic catalyst systems for ORR have been fabricated by various methods: the reduction of metal precursors by gas flowing [3] or a reducing agent [16], multistage incipient-wetness impregnation [15], self-assembly of Co-containing molecular films on Ag electrode [22], and electrodeposition [20,21,23]. Regardless of the advantages of electrodeposition such as simplicity and ease of control [20,21], only few studies on the use of electrodeposition for the synthesis of AgCo catalysts have been reported. Within confinement of our knowledge, all the previously reported electrodeposited AgCo catalysts were prepared by sequential deposition: i.e., Co was electroplated on an Ag-modified electrode.

In current study, we demonstrate a simple one-pot co-electrodeposition of AgCo. A series of AgCo catalysts with diverse Ag to Co ratios were electroplated simultaneously on glassy carbon (GC) electrodes in the deposition solutions containing Ag precursor, Co precursor, Triton X-100, and 0.3 M KNO₃ aqueous solution by varying the ratio of Ag and Co precursor concentrations. Their morphological structures and contents were characterized, and ORR activities were examined in 0.1 M NaOH solution. AgCo electrodeposited in the deposition solution with Ag:Co precursor ratio of 1:7 showed the best ORR activity. The deposition mechanism was further investigated by adjusting the deposition time. The corresponding ORR activities of AgCo depending on the deposition time were compared with that of bare Pt.

2. Experimental

2.1. Materials

Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), silver nitrate (AgNO₃), potassium nitrate (KNO₃), sodium hydroxide (NaOH, pellets, ≥98%, ACS reagent), Nafion and Triton X-100 were from Sigma Aldrich. All the chemicals were of analytical-reagent grade and used as received without further purification. All aqueous solutions were prepared using deionized water (resistivity ≥ 18 MΩ cm).

2.2. Solutions and electrodes

Before electrodeposition, glassy carbon rotating disk electrodes (GC RDE, 3 mm in diameter, Bioanalytical Systems, Inc.) were polished with 0.3 μm alumina slurry on a wet polishing cloth (Mark V Lab). The electrodes were cleaned and sonicated in distilled water for 5 min to remove the slurry residue. Silver cobalt (AgCo) thin films were fabricated in a similar method to a previous work described for nanoporous Pt [24]. AgCo was electroplated on the GC RDE by applying a constant potential of –0.57 V (vs. SCE) with a rotation rate of 100 rpm until the total deposition charge approached to 0.042C in a mixture of the metal precursors, 0.3 M KNO₃ aqueous solution, and Triton X-100 (5:45:50 in wt%). A series of AgCo thin films were fabricated by varying the metal precursor ratio of silver (AgNO₃) and cobalt (Co(NO₃)₂·6H₂O), i.e., Ag precursor:Co precursor = 1:χ (χ = 3, 4, 5, 6, 7, 8 and 11), which are denoted as Ag₁Co_χ. In fact, the molar ratio of the precursor concentrations ([Ag⁺]:[Co²⁺]) in each deposition solution was 1:3 (0.048 M:0.144 M), 1:4 (0.038 M:0.150 M), 1:5 (0.031 M:0.154 M), 1:6 (0.026 M:0.157 M), 1:7 (0.022 M:0.159 M), 1:8 (0.020 M:0.160 M), and 1:11 (0.015 M:0.160 M), respectively. For comparison, pure Ag- and Co-modified electrodes were prepared in similar deposition solutions to the AgCo deposition solutions but containing 5 wt% of either Ag or Co precursor only instead of a mixture of Ag and Co precursors. The applied potentials were 0 V for Ag and –0.85 V for Co (vs. SCE). For the deposition mechanism study, Ag₁Co₇ was electroplated depending on the deposition time (*t* = 5, 10, 50, 100, 150, 200 and 250 s) in the deposition solution with 1:7 ratio of Ag precursor to Co precursor. These catalysts are denoted as Ag₁Co₇-*t* (*t* = corresponding deposition time). A Pt wire and a saturated calomel reference electrode (SCE) with 3 M KNO₃ double junction were used as the counter electrode and reference electrode, respectively. All electroplating process was performed at 40 °C after activating the deposition solution at 60 °C using a refrigerating/heating bath circulator (RW-0525G, JEIO TECH). In the case of pure Ag, the electrodeposition was proceeded at 30 °C without the activation step to regulate the Ag reduction rate properly (*vide infra*) [25]. To extract the used Triton X-100 from the electrodeposited AgCo films, the as-prepared electrodes were immersed in deionized water being magnetically stirred, while replaced with fresh water every 3 h for 4–5 times.

2.3. Electrochemical and physical characterization

For the electrochemical characterization, 10.0 μL of 0.05 wt% Nafion solution was applied and dried on the electrode to secure AgCo thin film on the GC electrode surface. The catalytic activity for ORR was examined in an O₂-saturated 0.1 M NaOH aqueous solution by performing RDE voltammetry at various electrode rotating speeds (from 100 to 3600 rpm) using RDE-2 rotator (BASi, Bioanalytical Systems) and electrochemical analyzer (CHI 730D). A Pt wire and a SCE were used as the counter electrode and reference electrode, respectively. For stability test of Ag₁Co₇-200, the RDE voltammetry curves for ORR between 0 V and –0.8 V were recorded repetitively in an O₂-saturated 0.1 M NaOH with a scan rate of 10 mV s^{–1} and a rotation rate of 1600 rpm. The steady-state current densities measured at every RDE 100 runs were compared upto 700 repetitive runs. The geometric surface area (GSA) of each AgCo was measured in 5 mM ferrocene in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆)/acetonitrile using chronocoulometry (CC). All the RDE curves were normalized to the corresponding electrode GSA to obtain current density vs. potential curves.

The structures and compositions of AgCo thin films were characterized by scanning electron microscopy (FE-SEM, Jeol JSM-6700F), high-resolution transmission electron microscopy (HR-TEM, Jeol JEM-2100F), energy dispersive spectrometer (EDS) operating at

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