DOI: 10.1002/((please add manuscript number))

Article type: Communication

Oxygen Reduction at Very Low Overpotential on Nanoporous Ag Catalysts

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Keywords: (Electrocatalyst, Oxygen reduction, Nanoporous, Energy conversion, Fuel cell)

Electrochemical reduction of oxygen in alkaline environment is of tremendous importance for many electrochemical devices that are directly related to efficient energy conversion and storage applications. Among those applications, alkaline fuel cells (AFC) are promising future power sources due to the recent progress on hydrogen oxidation reaction (HOR) catalysts¹ and hydroxide exchange membranes;² lithium (Li)-air and zinc (Zn)-air secondary batteries are advanced energy storage devices for future electric vehicles and electrical grid of solar and wind power plant providing much higher capacity than current state-of-the-art lithium ion batteries.³⁻⁵ However, the successful large-scale implementation of these technologies relies on the development of active and stable oxygen reduction reaction (ORR) catalysts.

In the past few decades, a large number of catalysts have been investigated for electrocatalytic oxygen reduction in alkaline.⁶⁻⁹ To date, the precious metal platinum (Pt) has shown the

benchmark ORR activity in alkaline media. As a potential Pt replacement, silver (Ag) has been more thoroughly studied compared to other catalysts due to its relatively high activity, abundance and low cost.¹⁰⁻¹⁴ In addition, Ag is more stable than Pt in base as the equilibrium potential of Ag/Ag₂O being ca. 200 mV higher than that of Pt/PtO.¹⁵ Nevertheless, the ORR half-wave potential ($E_{1/2}$), which is commonly used to evaluate the electrocatalytic activity of a catalyst,^{16, 17} is ca. 200 mV lower for Ag than for Pt in rotating-disk electrode (RDE) polarization studies. Research efforts have been devoted to the engineering of nanostructured Ag catalysts, *i.e.* nanoparticles and nanowires, for achieving larger surface area and beneficial finite-size effect.¹⁸⁻²¹ Despite progresses, the performance of Ag is still not comparable with the commercial state-of-the-art carbon-supported Pt (Pt/C) catalyst.

Here we report a monolithic nanoporous Ag (np-Ag) material, synthesized using the dealloying method, as high-performance catalysts for ORR in alkaline media. As shown in **Scheme 1**, when there is insufficient potential input, the O₂ molecules are more likely to rebound off from a planar electrode surface (*i.e.* bulk polycrystalline metal, films made from nanoparticles or nanowires) before they could be reduced. In contrast, they are more likely to be trapped inside the monolithic nanoporous structure, contacting with catalytic surface for multiple time, which greatly enhances the chance for them to be fully reduced. As a result, the np-Ag catalyst is able to achieve an equivalent or better ORR performance than the state-of-the-art Pt/C catalyst at low overpotentials, which is most desired in electrochemical energy applications for maximizing efficiency.

Scheme 1. Representation of ORR on a planar electrode surface (left) and a monolithic nanoporous electrode surface (right) at low overpotentials.

The monolithic np-Ag catalysts were synthesized from Ag-Al solid solution precursors after a two-step dealloying process using aqueous HCl solutions, as reported in our previous work.²² By selectively leaching out Al from the Ag-Al alloy, the remaining Ag atoms diffused along the alloy-electrolyte interface at the etch front to form a three-dimensional nanoporous structure. Typical scanning electron microscopy (SEM) images of the as-synthesized np-Ag are shown in **Fig. 1 a**. The ligament size of np-Ag is around 100 nm, while the size of the pores extends to a few hundred nanometers. The high-resolution transmission electron microscopy (HRTEM) image (Fig.1 b) exhibits uniform lattice fringes. Both techniques suggest that the resulting np-Ag is highly crystalline, which is further confirmed by powder X-ray diffraction (PXRD) analysis (Fig.1 c). Additional SEM studies confirm that the resulting nanoporous structure is coherent throughout the material (Fig. S1), and no Al residue was detected in either X-ray photoelectron spectroscopy (XPS) (Fig. S2) or energy-dispersive spectroscopic analysis (Fig. S3).

Fig. 1 a) SEM image of an np-Ag dealloyed in 5 wt% HCl for 15 minutes and further in 1 wt% HCl for 30 minutes. b) Corresponding HRTEM with visible lattice fringes. c) PXRD patterns of the Ag-Al solid solution precursor (blue line), the dealloyed np-Ag (pink line), and Ag standards (grey line).

To evaluate the ORR catalytic activity, np-Ag was accommodated into a rotating disk electrode (RDE) setup and was tested in oxygen-saturated 0.1 M KOH electrolyte. In order to suppress the capacitive current due to the enhanced surface area of np-Ag, the ORR polarization curves were measured potentiostatically by fixing the potential until a steady current value was reached (Fig. S4).²³ As shown in **Fig. 2 a**, the np-Ag catalyst exhibited a significantly enhanced ORR activity with a more positive onset potential and higher current than that of a bulk polycrystalline Ag (bulk-Ag). Reflected by half-wave potential ($E_{1/2}$) values, the measured $E_{1/2}$ of np-Ag is 0.86 ± 0.01 V vs. RHE, which is 120 mV higher than that of bulk-Ag (0.74 ± 0.01 V vs. RHE). In comparison with Pt/C, the np-Ag exhibited a dramatically improved onset ORR potential of ca. 100 mV; at the low overpotential regime that is more desired for practical applications (> 0.85 V vs. RHE), the ORR current of np-Ag

substantially exceeded that of Pt/C, proving the essential role of the monolithic nanoporous structure in enhancing efficiency of reaction sites at low overpotentials. The controlled experiment of np-Ag using Ar-saturated electrolyte ensured that the measured ORR polarization curve stands for the true performance of np-Ag (Fig. 1 a). The kinetic currents of np-Ag, Pt/C and bulk-Ag were obtained using Koutecky-Levich equation and incorporated into the Tafel plots shown in Fig. 2 b, where the mass-transport corrected activities could be compared. In addition to the overwhelmingly larger currents than those of bulk-Ag, the np-Ag catalyst also exceeded Pt/C with a significant enhancement at low overpotential region (e.g., 0.9 V vs. RHE). Such outstanding performance at very low overpotentials can be mostly likely attributed to the reaction-promoting electrode architecture and the large surface area. In order to perform a Koutecky-Levich analysis on np-Ag, the rotation-rate-dependent polarization curves of np-Ag were measured (Fig. 2 c). The number of the electrons transferred (n) was estimated to be at least 3.5 from the slopes (k) of the Koutecky-Levich plots (Fig. 2 c inset) according to Equation S1.²⁴ It should be noted that the diffusion coefficient of O₂ inside the nanopores is expected to be smaller than that in bulk electrolyte which is adapted for estimation. Therefore, the calculated n of being 3.5 only stands for the lower bound of its true value. It is very likely that the number of the electrons transferred for np-Ag is close to 4, i.e., a full reduction of O₂ to 2O²⁻.

Fig. 2 a) ORR polarization curves of np-Ag, Pt/C and bulk polycrystalline Ag. The polarization curve of np-Ag was also measured in Ar-saturated electrolyte. Rotation rate: 1600 rpm. b) The corresponding Tafel plots. c) ORR polarization curves at different rotation rates. The inset shows the corresponding Koutecky-Levich plots at different potentials.

In addition to the enhancement in surface areas, we also explored the role of highly curved internal surface in the np-Ag particles using density functional theory (DFT) calculations. The surfaces of bulk Ag is most likely dominated by the closely-packed (111) faces that are thermodynamically stable for the face centered cubic (FCC) structure. As shown in Table S1, the OBE values are 3.53 eV on Ag(100), 3.79 eV on Ag(100) and 4.06 eV on Pt(111). The DFT results suggest that the oxygen binding energy (OBE) on a step Ag(110) surface is similar as that on a flat Ag(111) surface and slightly lower than that on a flat Ag(100) surface. Previous studies have revealed that the ORR activity can be correlated to the OBE on different surfaces.²⁵ However, in the case of nanoporous Ag case, the observed enhancement is mainly due to the nanoporosity instead of optimal OBE. The experimental assessment of specific activity of np-Ag is difficult because the reduction reaction usually only occurs near the outermost geometric surface,²³ although its electrochemical surface area (ESA) can be measured using electrochemical monolayer oxidation with OH⁻ in an Ar-saturated KOH electrolyte (Fig. S5).²⁶

The long-term stability was assessed by a US Department of Energy (DOE) protocol for accelerated aging in the RDE three-electrode cell configuration.²⁷ The np-Ag catalysts were aged by repeated 5000 potential cycling between 0.6 - 1.0 V vs. RHE at 50 mV s⁻¹, and the ORR polarization curves were recorded before and after such process. As shown **Fig. 3**, np-Ag catalyst exhibits a remarkable durability preserving the high kinetic activity, while the state-of-the-art Pt/C is known to lose a substantial amount of activity due to the dissolution of Pt surface atoms and agglomeration of Pt particles through surface oxidation/reduction processes.¹⁷

Fig. 3 ORR curves and (inset) corresponding Tafel plots of np-Ag before and after 5,000 potential cycles between 0.6 and 1.0 V vs. RHE.

In summary, np-Ag catalyst was synthesized and evaluated for ORR in alkaline electrolyte. The monolithic nanoporous structure is expected to promote the reaction rate at low overpotentials by improving the interactions between O₂ molecules and catalyst surfaces. The np-Ag catalyst exhibits higher ORR activity at low overpotential regime and better stability in the alkaline electrolyte than the state-of-the-art Pt/C catalysts. Its activity also exceeds that of other nanostructured Ag catalysts including nanoparticles and nanowires.^{15, 20, 21} The np-Ag catalyst provides a promising alternative to replace Pt-based catalysts in alkaline media without sacrificing any ORR activity, which is crucial for the development of low-cost and high-performance alkaline fuel cells and metal-air batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

† Yang zhou and Qi Lu contributed equally to this work. Authors at University of Delaware are grateful for financial support from the National Science Foundation Faculty Early Career Development (CAREER) Program (Award No. CBET-1350911) and the University of Delaware Research Foundation Strategic Initiatives (UDRF-SI) Grant. Authors at Columbia University acknowledge support from the US Department of Energy (DE-FG02-13ER16381).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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A monolithic nanoporous silver catalyst is developed to achieve a better performance than platinum at very low overpotentials for oxygen reduction reaction in alkaline conditions. Benefited from the reaction-promoting electrode architecture and the enhanced surface area, such nanoporous silver catalyst exhibited a three-fold improved activity than that of commercial state-of-the-art platinum carbon catalysts at 0.85 V vs. RHE.

Keyword

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Oxygen Reduction at Very Low Overpotential on Nanoporous Ag Catalysts

ToC figure

Supporting Information

Oxygen Reduction at Very Low Overpotential on Nanoporous Ag Catalysts

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Experimental methods

Preparation for precursor materials

Al₈₀Ag₂₀ precursor alloys were made by co-melting pure Ag (Alfa Aesar, 99.9%) and Al (Alfa Aesar, 99.99%) in a home-build arc-melter under an argon atmosphere. The resulting alloy ingot was annealed at 546 °C for 12 hours, followed by a rapid quenching process using a water/ice mixture bath to suppress the Ag₂Al intermetallic compound phase. After the removal of the surface rust using sandpaper (240 Grit), pure α -Al(Ag) phase was achieved.

Preparation for catalyst materials in rotating disk electrode (RDE) setup

Nanoporous Ag (np-Ag) electrode: The as-quenched alloy ingot was machined into a disk with diameter of 5 mm and thickness of about 0.2 mm. A two-step de-alloy process was adopted to leach out the Al, resulting in a monolithic np-Ag disk.¹ The np-Ag disk was rinsed with deionized water for multiple times and mounted in a custom-made exchangeable RDE apparatus (Pine Instruments Company).

Pt/C electrode: 10 mg of the commercial Pt/C (TKK, 48.8 wt.%) was dispersed in 10 mL deionized water + 10 mL isopropyl alcohol (Sigma Aldrich) + 5 wt.% Nafion solution (DuPont) and sonicated in a water/ice mixture bath for 30 minutes. 10 μ L of the dispersions were deposited on the surface of the glassy carbon electrode and dried under ambient conditions.

Structural characterizations

Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku Ultima IV X-ray diffractometer with Cu K α radiation. Refinement of the PXRD patterns was conducted using the Rietveld approach implemented in Rigaku's software package PDXL. Scanning electron microscopy (SEM) studies were performed with a JEOL JSM-6330F. X-ray photoelectron spectra were obtained using a Phi 5600 XPS system. Transmission electron microscopy (TEM) studies were performed with a JEOL JEM-2010F using an accelerating voltage of 200 kV.

Electrochemical measurements

A standard three-electrode glass cell equipped with a Pt wire counter electrode and an Ag/AgCl reference electrode was employed for electrochemical characterizations. All electrochemical characterizations were performed using a multichannel potentiostat (VMP2, Princeton Applied Research). The potential scale was calibrated to a reversible hydrogen electrode (RHE), and all potentials are reported with respect to RHE. RHE calibration was performed before each characterization in a hydrogen-saturated 0.1 M KOH electrolyte using a Pt RDE as working electrode.

The oxygen reduction reaction (ORR) was conducted in an oxygen-saturated 0.1 M KOH electrolyte with rotation speed of 400, 900, 1600 and 2500 rpm. The polarization curves for bulk polycrystalline Ag and Pt/C catalysts were obtained at a potential scan rate of 20 mVs⁻¹. ORR curves of np-Ag were obtained potentiostatically by fixing the potential until a steady current value was reached, typically 5 min for potentials less than 0.5 V vs. RHE and 2 min for the rest. Data points were collected every 100 mV in the diffusion-limited potential region and every 20 mV or 10 mV in the mixed kinetic-diffusion-limited potential region.

The electron transfer number n is determined by following equation:

$$n = \frac{1}{0.62kFD_0^{2/3}\nu^{-1/6}C_0} \quad (1)$$

where k is the fitted slope from Koutecky-Levich plots, F is the Faraday's constant, D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.93 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($1.09 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}$) and C_0 is saturation concentration of O_2 in 0.1 M KOH at 1 atm O_2 pressure ($1.26 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$).^{2,3}

The electrochemical surface area (ESA) measurement of Ag catalysts was performed in an Ar-saturated 0.1 M KOH electrolyte. After electrochemical reduction at -0.4 V vs. RHE for 10 min, the Ag catalysts were oxidized at 1.15 V vs. RHE, which was believed to only form a monolayer of Ag_2O or $AgOH$, corresponding to a charge of about $400 \mu\text{C cm}^{-2}$.⁴ By comparing the amount of electrons passed during the oxidation process, the ESA of different Ag catalysts can be obtained.

Computational methods

Self-consistent periodic density functional theory (DFT)^{5,6} calculations were performed using the Vienna Ab-Initio Simulation Package (VASP).^{7,8} A plane wave cut-off energy of 400 eV and $5 \times 5 \times 1$ Monkhorst-Pack⁹ grid were used for total energy calculations. All the computations were conducted in spin unrestricted manner using ultrasoft pseudopotentials.¹⁰ Electronic exchange and correlation effects were described within the generalized gradient approximation (GGA) using PW91 functionals.¹¹ Ionic positions were optimized until Hellman-Feynman force on each ion was smaller than $0.01 \text{ eV/\AA}$. Pt(111), Ag(111), Ag(100) and Ag(110) surfaces were modeled using a 2×2 surface slab cell with four atoms per surface layer and four layers of atoms. A vacuum layer of $\sim 12 \text{ \AA}$ thick was added in the slab cell along the direction perpendicular to the surface in order to avoid the artificial interactions between the surface and its periodic images. During geometry optimization, the atoms in the top two layers were allowed to relax whereas the atoms in the bottom two layers were fixed. The oxygen binding energy is calculated as the difference between the energy of the slab with

adsorbed O and the energy of the isolated clean slab and atomic O. Negative binding energy indicates energetically favorable interaction between the slab and adsorbed O.

Fig. S1: Low-magnification SEM image of an as-prepared np-Ag electrode. Inset: SEM image at the center of the cross-section.

Fig. S2: XPS Ag 3d and Al 2p spectra for $\text{Ag}_{20}\text{Al}_{80}$ precursors and as-prepared np-Ag. The np-Ag sample shows typical Ag metal spectrum with peak separation of 6 eV and no Al residuals. The precursor sample shows a peak at 72.24 which corresponds to Al and a peak at 75.6 eV which usually corresponds to Al_2O_3 . The associated Ag spectrum shows higher binding energy peaks that may result from forming Ag-Al-O oxide compounds.

Fig. S3: EDX spectrum of **a**, $\text{Ag}_{20}\text{Al}_{80}$ precursor and **b**, dealloyed nanoporous Ag showing no detectable Al residue.

Fig. S4: Examples of potentiostatic ORR measurement where the current is steady for about 100 seconds at several different potentials with a rotation rate of 1600 rpm.

Fig. S5: **a**, A typical cyclic voltammogram of Ag within the potential window of 0 to 1.60 V vs. RHE.

The current peak observed at about 1.15 V corresponds to a monolayer formation of Ag₂O or AgOH.

Current transient at constant potential (1.15 V vs. RHE) for nanoporous Ag (**b**) and polycrystalline Ag (**c**). To use electrochemical surface area for estimating specific performance, there is an implicit

assumption that the surface area which is accessed by OH⁻ can also be accessed by O₂ during ORR.

While it is likely the case for bulk-Ag electrode or other planar electrodes composed by Ag nanoparticles or nanowires, it may not be true for np-Ag in which the reduction reaction may only occur near the outermost geometric surface.¹² Having that in mind, it is not surprising to see a “lower specific activity” of np-Ag (24 μA cm⁻² at 0.9 V vs. RHE) comparing to that of bulk-Ag (55 μA cm⁻²). It only suggests that at least half of np-Ag surfaces were not utilized in the ORR due to the diffusion of low-concentration O₂ molecules.

Table S1: Oxygen binding energy (OBE) (in eV) on various adsorption sites on 2×2 Pt (111), Ag(111), Ag(100) and Ag(110) surfaces. Bold number on each surface represents the most thermodynamically stable site. The illustrations of the various binding sites are shown in Fig. S6.

site	Pt(111)	Ag(111)	site	Ag(100)	site	Ag(110)
fcc	-4.06	-3.53	hollow	-3.79	fcc-hollow	-3.51
hcp	-3.64	-3.42	top	-1.90	hollow	-3.47
top	-2.71	-2.01	bridge	-2.96	top	-2.01
bridge	NS	NS			long-bridge	-3.41
					short-bridge	-3.09

NS = not stable

Fig. S6: Various adsorption sites on 2×2 Ag(111), Ag(100), and Ag(110) surfaces.

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