A catalyst design for selective electrochemical reactions: direct production of hydrogen peroxide in advanced electrochemical oxidation†

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Hydrogen peroxide production by enhanced electrocatalysts is an attractive alternative to the present commercial process. While the subnano/atomic dispersion in noble metal nanocatalysts is known to strongly enhance their catalytic efficiency and chemoselectivity, their excessive surface energy and consequent coarsening seriously compromise their physical/chemical stability. Here, we report a subnano/atomically dispersed Pt–Ag alloy (by a simply modified polyl process) that is resistant to agglomeration/Ostwald ripening. This catalyst does not follow a conventional four-electron oxygen reduction reaction (ORR) but selectively produces H2O2 without excessive degradation of its activity. We clarified the role of the alloying element, Ag, as follows: (1) selective activation of two-electron ORR by inhibiting O2 dissociation and (2) suppression of H2O2 decomposition by preventing the H2O2 adsorption. The present approach provides a convenient route for the direct generation of H2O2 as a simple byproduct of electricity generation by fuel-cell systems.

Introduction

Hydrogen peroxide (H2O2) is an environmentally friendly chemical oxidant and potential energy carrier used in the pulp/paper industry and for water treatment. It is one of the most widely employed chemicals, and its annual production by centralized reactors is over 3 million tons. Presently, the most widely adopted production process is sequential hydrogenation-oxidation of anthraquinone. Since these processes are energy intensive and complex, alternative approaches for the direct synthesis of H2O2 through a catalytic process have been extensively studied. Among such approaches, the electrochemical synthesis of H2O2 is particularly attractive, not only since it allows ambient conditions but also since it is free from the critical flaw of solution-based production, i.e., the peroxide disproportionational reaction, which is the spontaneous decomposition of H2O2 into water and oxygen (Fig. S1†). Thus, the electrochemical synthesis of H2O2 finds its greatest advantage in advanced oxidation processes (e.g., electro-Fenton), where H2O2 generation is accompanied by immediate on-the-spot consumption.

The most widely employed catalyst for the electrochemical synthesis of H2O2 is Pt due to its superior activity, selectivity and physical/chemical stability. For example, Yang et al. employed Pt single atoms supported on TiN, and Choi et al. proposed an atomically dispersed Pt–S electrocatalyst. Refining particles to the nanoscale or even to the atomic scale drastically enhances the catalytic activity since it reduces metal–metal coordination, which suppresses chemical reactions encompassing multiatom sites. However, in the case of Pt single atom, it must be deposited on the support materials in the oxide state.

To avoid this issue, the catalyst has to be synthesized another metal–organic bond such as Pt–S. Moreover, such an approach...
suffers from critical drawbacks, such as accelerated agglomeration and Ostwald ripening, which are triggered by the chemical/thermal/electrochemical energy input.\textsuperscript{23–26} This input leads, in the case of Pt, to an accelerated four-electron reaction resulting in undesirable \( \text{H}_2\text{O} \) generation.\textsuperscript{27} Minimizing the loading to below 1 wt% might be a possible choice to overcome this problem but is accompanied by deterioration in the catalytic performance.\textsuperscript{14–28}

On the other hand, Hg-based alloy nanoparticles were employed as catalyst with high \( \text{H}_2\text{O}_2 \) selectivity.\textsuperscript{29} However, such catalysts are also accompanied by deterioration in the catalytic performance due to its few active sites (low Pt atomic ratio). Moreover, Hg is extremely toxic and can cause both chronic/acute poisoning.\textsuperscript{29,30} In some cases, non-metal based materials such as highly oxidized carbon structure were adopted as catalyst. However, since the operate condition was confined to the alkaline condition, they could not be used in fuel-cell devices with proton exchange membrane (PEM).\textsuperscript{31} Thus, designing a new catalyst with improved performance is in a strong demand.

Here, we report a subnano/atomic scale Pt–Ag alloyed catalyst with drastically improved electrochemical stability and a strongly suppressed multi-Pt-site reaction. We also clarified the relevant mechanism by focusing on the role of the alloying element, i.e., Ag. We demonstrated that Ag plays a crucial role in an oxygen reduction reaction (ORR) under a weak acidic environment, avoiding the conventional four-electron path to \( \text{H}_2\text{O} \) generation and enabling a dominant two-electron path to \( \text{H}_2\text{O}_2 \) generation, thereby preventing its decomposition. The feasibility of Pt–Ag for large scale application was evaluated under the H-cell and PEM based single-cell condition. The present approach provides a convenient route for simple direct generation of \( \text{H}_2\text{O}_2 \) as a byproduct of electric power generation in fuel cells and provides an effective route for the direct removal of various organic pollutants in synthetic and actual wastewater. We demonstrated application of the present Pt–Ag catalyst for the removal of microcystin-LR and microcystin-RR, the toxic substances generated by green algae. We demonstrated the application simultaneously with electric power generation in fuel cells under the electro-Fenton process, where \( \text{H}_2\text{O}_2 \) production was accompanied by on-the-spot consumption. This finding may practically provide insight into the preparation of improved electrocatalysts for \( \text{H}_2\text{O}_2 \) production and various application. The main text of the article should appear here with headings as appropriate.

**Experimental details**

**Chemicals**

Platinum(IV) chloride, silver nitrate, ethylene glycol starch and cysteamine were purchased from Sigma-Aldrich (USA). Ketjen Black 300J was supplied by LION (Japan). A hydrogen peroxide test kit (thiosulfate and ammonium molybdate) was purchased from Hach (USA). A Pt/C reference of Pt 40 wt% was purchased from Alfa Aesar. Microcystin-LR and -RR were purchased from AAA.

**Preparation of Pt–Ag alloy catalysts**

For the Pt–Ag alloy/C, silver nitrate and platinum chloride were dissolved in 10 mL of ethylene glycol, which was subsequently heated to 50 ºC for 30 min with vigorous stirring. One hundred mg of carbon black (Ketjen black 300J) and 10 mg of cysteamine were ultrasonically blended in 20 mL of ethylene glycol. Cysteamine was used as an anchoring agent. The prepared carbon–cysteamine solution was added to the precursor solution and subsequently heated to 120 ºC for 1 hour in \( \text{N}_2 \) atmosphere. The reaction mixture was cooled to room temperature, filtered, and washed with a mixture of ethanol and deionized water several times. The final product was dried at 60 ºC. The Ag/C nanoparticles were synthesized using the general poloyl process.

**Physical characteristics**

The nanostructure of the synthesized Pt–Ag particles was observed by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM, Titan). The Pt–Ag nanoparticle size distributions were analyzed using ImageJ software, and the obtained profiles were fitted using Gaussian function. Ten HAADF-STEM images were taken for each sample, from which five hundred particles were selected for the particle size measurement. For atomic-resolution elemental mapping, the high-resolution energy dispersive spectroscopy (EDS) was taken on the FEI TALOS with a probe aberration corrector operated at 200 keV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out using an ICP-OES 725 (Agilent) after pretreatment of samples at 250 ºC in aqua-regia for determination of metal contents. The in situ/orapendo ICP-OES and ICP-MS were performed to confirm the stability of Ag and Pt during long-term operation. X-ray photoemission spectroscopy (XPS) was performed using K-Alpha (Thermo Scientific) with a microfocused X-ray probe. The \( Pt_{4d} \) and \( Ag_{3d} \) peaks were analyzed, adopting the specific peak area ratios of 3 : 4 and 2 : 3 relevant to the spin–orbit splitting, respectively.\textsuperscript{33} The employed binding energies were 70.8–71.0 eV for Pt,\textsuperscript{34} 71.4–71.6 eV for chemically shifted Pt\textsuperscript{0} (Pt–Ag), 368.3 eV for Ag\textsuperscript{0}, 367.4 eV for Ag\textsuperscript{+}, and 367.9–368.0 eV for chemically shifted Ag\textsuperscript{0} (Pt–Ag).\textsuperscript{35} The binding energy differences with respect to the spins for the elements were 3.35 eV (Pt) and 6.0 eV (Ag).\textsuperscript{36} The top-surface composition of the alloy nanoparticles was observed by synchrotron XPS at the 4D PES beam line of the Pohang Accelerator Laboratory (PAL) in the Republic of Korea. The crystallographic structure and average particle size were obtained by synchrotron X-ray diffraction (XRD) analysis at the 1D KIST beamline of the PAL; the Pt particle size was calculated from the (220) diffraction peaks.

The catalytic activity for the peroxide disproportionation reaction (PDR) was confirmed by dispersing 10 mg catalyst in a 50 mM Na\textsubscript{2}SO\textsubscript{4} solution with 10 mM H\textsubscript{2}O\textsubscript{2}. After a specified time, the solution was filtered, and the concentration of H\textsubscript{2}O\textsubscript{2} was analyzed by iodometry using a Hack peroxide test kit. The PDR in the absence of the catalysts was also observed following the same procedure for comparison.
Iodometry

The concentration of H₂O₂ generated from all electrochemical experiments was analyzed by iodometry. Iodometry is a redox titration where the elementary iodine indicates the end point. The hydrogen peroxide oxidizes iodide (I⁻) to iodine (I₂) in the presence of acid and ammonium molybdate catalyst.

\[
\text{H}_2\text{O}_2 + \text{K} \rightarrow \text{I}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \tag{1}
\]

The iodine concentration related to the initial amount of hydrogen peroxide by 1 : 1 stoichiometry. The presence of iodine is indicated by a brown color of the solution. The redox titration of iodine performed using sodium thiosulphate as a reducing agent.

\[
\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \tag{2}
\]

In the final stages of the thiosulfate solution, the color of solution has reached a pale, yellow color. The starch \([\text{C}_6\text{H}_{10}\text{O}_5\text{]_n}]\) indicator is used to determine the end point. Added starch forms a blue complex with minute amounts of triiodide ions that are formed only in the presence of both iodine and iodide in solution. Finally, the blue color disappears when the iodine is completely reduced to iodide.

XAFS analyses

The Pt L₃-edge XAFS were obtained for the synthesized catalysts at the 1D KIST beamline of the PAL. The measurements were made in fluorescence mode utilizing a Si(111) channel-cut monochromator. The photon energy scanning steps were adjusted to an incident radiation energy step of 1.0 eV and a photoelectron wavenumber of 0.03 Å⁻¹ in the XANES and EXAFS regions, respectively. The measured XAFS spectra were calibrated using Pt foil to guarantee no shift in the edge energy. The Ag K-edge XAFS was measured at the 1C beamline of the PAL under the same experimental conditions.

The XANES data were analyzed using Athena (Demeter ver. 0.9.20). In the fitting, the height for the arctangent function corresponding to the transition to the continuum level was fixed to one to maintain consistency in the analysis. For EXAFS analysis, Artemis (also implemented in Demeter ver. 0.9.20) was utilized after data processing using Athena. The background removal was performed to extract the EXAFS signal for R_bkg = 1–1.2 Å. The EXAFS data were transformed using the Kaiser–Bessel function. The many-body reduction factor (S₀²) for Pt was determined to be 0.86 from the curve fit of the EXAFS of Pt foil. The statistical quality of the curve fit with the proposed models can be determined from the R-factor and the χ² function available in the refinement. To predict the component distribution of the alloy cluster, the short-range order parameter (η) was calculated by the following equations using the coordination numbers (CNs) obtained from the EXAFS simulation.

\[
x = N_{\text{pt}}/N_{\text{total}} \tag{3}
\]

\[
\eta = 1 - \frac{\text{CN}_{\text{Pt–Ag}}}{(1-x)(\text{CN}_{\text{Pt–C(0)}} + \text{CN}_{\text{Pt–Pt}} + \text{CN}_{\text{Pt–Ag}})} \tag{4}
\]

DFT calculations

We carried out density functional theory (DFT) calculations using the Vienna ab initio simulation package. The exchange correlation functional was described by the revised Perdew–Burke–Ernzerhof (RPBE) functional with the general gradient approximation (GGA) method. We adopted pseudopotentials generated under the projector-augmented wave (PAW) method. The cut-off energy for the plane wave basis was set to 500 eV, and all the structures were optimized with force criteria under 0.01 eV Å⁻¹. The lattice constant of the periodic cell was set to 18 × 18 × 18 Å³ to avoid interaction between nanoparticles in different cells. Considering the particle size (~1.5 nm) measured in the experiment, we built a nanoparticle with 55 atoms by varying the mixing ratios between the pure Ag and the pure Pt.

Molecular dynamics for H₂O₂

We further investigated the dissociation of H₂O₂ at various nanoparticle compositions using ab initio molecular dynamics (AIMD). The simulation temperature was set to 300 K, and the simulation was conducted for 10 ps with a time step of 1 fs. We compared the dissociation behaviors of one H₂O₂ molecule on Pt and Pt–Ag alloyed nanoparticles.

Electrochemical measurements

The rotating ring disk electrode (RRDE) tests were performed using CHI 600D bipotentiostat (CH instrument) in a three-electrode system with a Pt wire counter electrode (Pine Research Instrumentation, AFCTR5) and a Ag/AgCl reference electrode (Bioanalytical Systems, MF-2052). All experiments were performed in a 50 mM Na₂SO₄ solution with pH adjustment using H₂SO₄. The measured potentials were reported versus the reversible hydrogen electrode (RHE) scale \((E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.197 \text{ V} + 0.0591 \text{ V pH})\). The working area of the glassy carbon disk was 0.247 cm². Prior to the RRDE experiments, catalyst inks were prepared by blending the catalyst in a mixture of DI water, ethanol and NaF solution. Twelve microliters of the catalyst ink were loaded onto the glassy carbon and dried at room temperature. The mass loading was 8 μgPt cm⁻². Linear sweep voltammetry (LSV) was carried out with a 5 mV s⁻¹ scan rate and 900 rpm rotating speed in an O₂-saturated electrolyte. The LSV responses are presented excluding the double layer capacitance of the carbon support by subtracting the currents measured in a N₂-saturated electrolyte. The number of electrons transferred \((n)\) and H₂O₂ selectivity were calculated from the RRDE measurements using eqn (5) and (6):

\[
n = 4 \times \frac{I_D}{I_D + I_R/N} \tag{5}
\]
\[ \text{H}_2\text{O}_2\% = 200 \times \frac{I_R/N}{I_D + I_R/N} \]  

(\( I_R \) = ring current, \( I_D \) = disk current, \( N \) = collection efficiency; 0.37) the activity of the peroxide reduction reaction (PRR) was confirmed by following the same method for the RRDE test, except for the use of an \( \text{N}_2 \)-saturated electrolyte containing 10 mM \( \text{H}_2\text{O}_2 \).

H-cell tests were performed using a 50 mM \( \text{Na}_2\text{SO}_4 \) solution (\( \text{pH} = 3 \)), and the anolyte and catholyte were separated by a Nafion 212 membrane (DuPont). Prior to the H-cell test, the catalyst inks were prepared by blending 10 mg of synthesized catalyst or Pt/C reference sample in a mixture of isopropanol alcohol, DI water and Nafion solution. The catalyst solutions were drop-coated onto carbon paper (geometric area = 1 cm\(^2\)). A Pt/C reference sample was used as the catalyst of the counter electrode. The catalyst loadings on the working and counter electrodes were 1 mg cm\(^{-2}\) and 2 mg cm\(^{-2}\), respectively. Two hundred ccms of \( \text{H}_2 \) and \( \text{O}_2 \) gas were injected into the anode and cathode, respectively. All H-cell experiments were performed under 0.2 V vs. RHE at room temperature.

**Single-cell measurement**

The electrodes were prepared by spraying catalyst ink on the gas diffusion layer (GDL). The catalyst ink was prepared by mixing 60 mg of the prepared catalyst and 400 mg of 5 wt% Nafion solution (Sigma-Aldrich) in 3.6 mL of isopropanol alcohol. All catalyst inks were ultrasonicated for 20 min to ensure uniform mixing and spray-coated using an airbrush over a GDL heated to 343 K on a heated vacuum plate. The prepared catalysts (Pt\(_{4}\text{Ag}_{0.1}\)/C; 1 mg cm\(^{-2}\)) and a commercial Pt/C catalyst (2.0 mg cm\(^{-2}\)) were deposited on the cathode and anode (with an area of 10 cm\(^2\)), respectively. Teflon cloth gaskets were used as the gas seal and for the insulation. A Nafion 212 membrane was used as the electrolyte and gas separator. To increase the diffusion of the produced \( \text{H}_2\text{O}_2 \), a 50 mM \( \text{Na}_2\text{SO}_4 \) solution with \( \text{pH} 3 \) was supplied to the cathode, respectively. All H-cell experiments were performed under 0.2 V vs. RHE at room temperature.

**Advanced oxidation (electro-fenton) process**

The electro-Fenton reactions were conducted by following the aforementioned H-cell test procedure, except for the use of a catholyte containing an organic pollutant (microcystin-LR and microcystin-RR); 5 ppm of the organic pollutant and 5 ppm of initial \( \text{Fe}^{3+} \) were introduced into the catholyte. Organic pollutants were quantified by chromatographic separation using an ultra-performance liquid chromatograph (UPLC) (Agilent 1290 Infinity series, Agilent Technology, Waldbronn, Germany) equipped with a triple-quadrupole mass spectrometer (6460 Jet Stream series, Agilent Technologies). A Zorbatrap Eclipse Plus C18 column (1.8 \( \mu \)m particle size, 2.1 \times 100 mm) was utilized as the stationary phase. The mobile phase was composed of 0.1% HCOOH in DI and 0.1% HCOOH in a \( \text{C}_2\text{H}_3\text{N} \) solution at a ratio of 70 : 30 (v/v) with a flow rate of 0.3 mL min\(^{-1}\). The analysis was conducted under isocratic conditions with an injection volume of 10 \( \mu \)L, a source voltage of 3.5 kV, and a column temperature of 35 °C.

**Results and discussion**

Structure and physical properties of Pt–Ag electrocatalysts. Subnanomter (or atomically dispersed) Pt–Ag alloy catalysts were synthesized by a modified polyol process (see Experimental section). The Pt and Ag loadings of all catalysts are summarized in Table S1.† Bright-field high resolution transmission electron microscopy (HR-TEM) images showed that Pt clusters with ca. 1 nm diameters were present in the Pt\(_{4}\text{Ag}_{0.1}\)/C sample (Fig. S2†). To further visualize the subnanometer/atomically dispersed Pt phase, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed (Fig. 1a–d) along with statistical particle size distribution analysis (inset figures in Fig. 1a–d). In contrast to the alloy samples, the Pt/C and Ag/C samples were composed of clusters of a few nanometers in diameter (Fig. S3† Pt/C and 4: Ag/C). In the Pt–Ag alloy samples, very small Pt–Ag clusters (\( \leq 1 \) nm) coexisted with atomically dispersed elements. The amount of atomically dispersed Pt–Ag phase was at a maximum in the Pt\(_{4}\text{Ag}_{0.1}\)/C sample (see additional STEM images in Fig. S5†). The subnanometer/atomically dispersed species showed no agglomeration under the irradiation of an electron beam (high energy of 300 kV) during the recording time (Movie S1†). Only thermal hoping to the neighboring sites was observed within the time scale. The macroscopic information of Pt–Ag catalysts was confirmed through XRD analysis (Fig. S6†). As a result, the particle size based on the XRD spectra was almost similar to those based on TEM analysis.

The atomic compositions of Pt and Ag in the alloyed electrocatalysts were determined by X-ray photoemission spectroscopy (XPS, Fig. 1e and f). The results indicated that the Pt–Ag phase was dominant in the Pt\(_{4}\text{Ag}_{0.1}\)/C sample, while other samples contained Pt oxide/dealloyed Pt peaks (separate Pt clusters or segregation in alloy particles). The Pt-Ag samples showed Pt\(_4\)\text{O}_{2}–Pt\(_0\)/Pt\(_4\)–Pt\(_{2}\)/Pt\(_{4}\)–Pt\(_{0}\) ratios of 56.9/10.0/33.1/0 (Pt/C), 60.6/18.2/9.1/12.1 (Pt\(_{4}\text{Ag}_{0.1}\)/C), 55.6/19.4/8.3/16.7 (Pt\(_{4}\text{Ag}_{0.05}\)/C), 11.5/7.7/3.8/77.0 (Pt\(_{4}\text{Ag}_{0.03}\)/C) and 15.6/18.8/3.1/62.5 (Pt\(_{4}\)Ag/C). X-ray absorption near-edge structure (XANES, Fig. S7†) also revealed that the white-line intensity and position of Pt\(_{4}\)/C corresponded to that of Pt\(_0\) (oxidation state = 0.58), while that in the other samples corresponded to a mixture of Pt\(_4\), Pt\(_2\) and Pt\(_0\) (oxidation state = 1.01–2.66).\(^{27,38}\)

In earlier reports, the oxidation state of atomically dispersed Pt was found to vary between +2 and +4.\(^{15,37,20,39}\) The escape depths of Pt\(_{4}\) and Ag\(_{4}\) for monochromated Al kx X-rays were approximately 6 Å and 13 Å, respectively, which are similar to the average particle size of the Pt–Ag samples. Therefore, synchrotron XPS was adopted for the top-surface analyses (Fig. S8†). The observed existence of Pt\(_4\)\text{O}_{2}–Pt\(_0\) and Ag\(_{4}\) on the top surface indicated that the metal particles chemically bonded with the supporting carbon and with functionalized oxygen.

Extended X-ray absorption fine structure (EXAFS) was used to analyze the nature of the alloying in the Pt–Ag electrocatalysts...
(Fig. 1g). EXAFS curve fitting indicated that the coordination number (CN) was maximized as 3.7 for the Pt$_3$Ag$_1$/C sample relative to that of the other samples (Table S2†). This result indicates that subnano/atomic alloying of the Pt–Ag alloy was optimized at that specific Pt/Ag ratio. In the case of Pt$_3$Ag$_1$/C, which had the finest particle size, the atomic distances of Pt–Pt and Pt–Ag were 2.55–2.60 Å and 2.90–2.95 Å, respectively, in contrast to the Pt–Pt distance of 2.72 Å for the sample with Pt segregation or dealloying.

We calculated the short range order parameter ($\eta$) from the values of CN$_{Pt-C\{O\}}$, CN$_{Pt-Pt}$, and CN$_{Pt-Ag}$ and the concentration of Pt atoms (Table S2†). The previous report on intermetallic compounds indicated that the parameter $\eta = -1$ when a host element was accompanied by alloying elements in every immediate neighboring site (homogeneity); $\eta = 0$ for fully disordered mixing among the constituent elements (disorder); and $\eta = +1$ for pairing between the same elements (segregation). For Pt$_3$Ag$_1$/C, the $\eta$ value (–0.7) was the closest to –1 among the samples, indicating optimized alloying. For the accurate confirmation of the atomic arrangement within particles, we conducted EDS mapping for Pt–Ag alloy catalysts and their results are shown in Fig. S9.† The shapes in which Pt and Ag of Pt$_3$Ag$_1$, and Pt$_2$Ag$_1$, are separated from each other in the particle were clearly visible. However, in the case of Pt$_3$Ag$_1$, it was possible to observe a shape that was randomly mixed in particles, which is consistent with the $\eta$ parameter obtained from EXAFS.

Electrochemical properties: two-electron ORR. The ORR performance was studied in an O$_2$-saturated 0.05 M Na$_2$SO$_4$ electrolyte (pH = 3), as shown in Fig. 2. Except for the Pt$_3$Ag$_1$/C and Pt–Ag samples, the onset potentials were between 0.75 and 0.86 V$_{RHE}$, which indicated simultaneous production of H$_2$O$_2$ (two-electron pathway) and H$_2$O (four-electron pathway). In contrast, for Pt$_3$Ag$_1$/C, the onset potential was 0.68 V$_{RHE}$ closely approaching the standard potential of H$_2$O$_2$ generation ($E^\circ = 0.69$ V$_{RHE}$) (Fig. 2a). Fig. 2b indicates the excellent H$_2$O$_2$ selectivity of the Pt$_3$Ag$_1$/C catalyst: well over 90% and approximately 70% for low and high overpotentials, respectively. In contrast, those of the other catalysts were below 50%. This difference indicated that a two-electron pathway ($n = 2.1$ at low overpotential, and $n = 2.6$ at high overpotential) was dominant in the ORR for Pt$_3$Ag$_1$/C, in contrast to the mixed two/four-electron pathways ($n \geq 3$) for the other catalyst samples. Since the four-electron ORR is well known to prevail on the non-alloyed Pt electrocatalyst, its absence with Pt$_3$Ag$_1$/C nanoparticles was attributed to the aforementioned uniform alloying with Ag. While both two/four-electron ORRs have identical first reaction steps, the second reaction step, i.e., O$_2$ adsorption, is different: additional H$^+$ induces O–O dissociation to form O–O$^*$ and O–OH$^*$ in the four-electron ORR, while it induces O–OOH$^*$ in the two-electron ORR (O$^*$ represents the adsorbed state). Thus, O–O dissociation is a pivotal step in selection between two/four-electron ORR pathways, which prompted our analyses to focus on the O$_2$ molecules adsorbed on nanoparticles to determine their bond lengths and adsorption configurations as follows.

To clarify the relevant roles of silver atoms in the alloy particles, we simulated the subnanometer structures of Pt and
the Pt–Ag alloy (Fig. S10:† Pt and Pt1Ag1 subnanoparticles). Pt1Ag1 nanoparticles were constructed by 3D positioning of Pt and Ag atoms to represent the alloying configurations. The O2 adsorption is the most stable at the edge sites.43 A variety of possible adsorption configurations are given in Fig. 3. First, the $E_a (E_a = E_{\text{NP-OO}} - (E_{\text{NP}} + E_{\text{OO}}))$ of Ag-NP was positive, i.e., $+0.06 \text{ eV}$, indicating that O2 adsorption on Ag-NP is an endothermic reaction and led us to exclude the Ag-NP from the analyses. The O2 adsorption energies on Pt-NP and Pt1Ag1-NP were negative, indicating the spontaneous adsorption of the O2 molecule, and the values were $-0.96 \text{ eV}$, $-1.32 \text{ eV}$ and $-0.46 \text{ eV}$, respectively. The bond lengths (which represent the bond strength) of Pt–O( O–O) on Pt-NP (Fig. 3a) were 1.97–1.98 Å (1.41 Å), indicating that O–O binding was stronger than Pt–O on the unstrained Pt surface. This result was also consistent with the report that O atom bonding to strained Pt was weaker than that to unstrained Pt.44 For O2 bonded to the Pt-NP and the segregation portion of Pt1Ag1-NP (Fig. 3a and b), the calculated O–O bond length was 1.41 Å and 1.43 Å, and the lengths of the two Pt–O bonds were similar, of which values are differed by 0.01 Å and 0.04 Å. In contrast, the calculated bond lengths for the O2 adsorbed on the alloyed portion of the Pt1Ag1-NP surface (Fig. 3c) differed greatly: 1.94 and 2.40 Å for Pt–O and Ag–O, respectively. The Pt–O bond changed little, while the Ag–O bond significantly weakened; the net result was that Ag alloying suppressed the O2 molecule dissociation. Such suppressed adsorption and strengthening of the O–O bond by Ag alloying are essential features that lead to the desired two-electron ORR path, as shown below.

In the four-electron ORR, the adsorbed O–O bond is broken to form O* and OH* when additional H* attach, and this is a well-known intermediate step in the ORR (Fig. 3d and e). In contrast, the present calculation indicates that H* attaching to the adsorbed O atom in PtAg-NP induces OOH* formation; i.e., the well-known intermediate reaction in the two-electron ORR (Fig. 3f) is due to the strengthened O–O bond (Fig. 3c). Ag alloying suppresses the breakage of the O–O bond, while the accompanying Pt atom keeps the adsorbed O2 molecule. Thus, the Ag–Pt coupled atomic site plays a critical role in OOH* formation.

Another important factor to consider in the electrochemical generation of H2O2 is the peroxide reduction reaction (PRR, H2O2(aq) + 2H+ + 2e− → 2H2O) and disproportionation reaction

Fig. 2 Electrocatalytic properties of Pt–Ag alloy catalysts. For comparison, commercial Pt/C and Ag/C were measured as reference electrocatalysts under the same condition. (a) ORR activities of the Pt–Ag alloy catalysts measured in O2-saturated 50 mM Na2SO4 solution with pH 3; rotation speed = 900 rpm, scan rate = 5 mV s−1. (b) H2O2 generation selectivity calculated from (c) the ring current of the RRDE measurements with a ring potential of 1.2 V_RHE. (d) The electron transfer (n) values.

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In general, the sequential decomposition of H$_2$O$_2$ on the surface of Pt is very fast. Therefore, reducing the adverse reaction greatly affects the yield of H$_2$O$_2$ in aqueous solution. To rule out a possible artifact origin of the high H$_2$O$_2$ yield on Pt–Ag alloy, we verified suppression of the PRR and PDR through an analysis employing a 10 mM H$_2$O$_2$ solution. As shown in Fig. 4a, the Pt–Ag alloy catalysts exhibit significantly lower currents and onset potentials for the PRR relative to the Pt catalyst. Furthermore, while the Pt catalyst induced a rapid drop in the H$_2$O$_2$ concentration when 10 mg catalyst was in the solution, the PDR activity was inhibited on the Pt–Ag alloy catalysts (Fig. 4b). For the rapid dissociation of H$_2$O$_2$ using metal NPs, H$_2$O$_2$ should be adsorbed through both of the electrochemical/non-electrochemical steps on the NPs. To study the dissociation of H$_2$O$_2$ on the atomic scale, we calculated the adsorption behaviors of H$_2$O$_2$ on Pt and Pt$_1$Ag$_1$ (Fig. 4c–h). On the Pt-NP, H$_2$O$_2$ exothermally dissociated to two OH groups adsorbed on two adjacent Pt atoms through three steps: (1) adsorption of one oxygen atom in H$_2$O$_2$ (Fig. 4c); (2) O–O bond breaking in H$_2$O$_2$ (Fig. 4d); and (3) adsorption of dissociated OH on the neighboring atomic site (Fig. 4e). The results of the relevant MD simulation are given in Movies S2 and S3†. Each movie shows a different H$_2$O$_2$ dissociation path depending on the initial configuration in which H$_2$O$_2$ dissociated into two OH$^*$ (Movie S2†) or H$^*$ and H$_2$O (Movie S3†) as soon as H$_2$O$_2$ was bound to Pt. In contrast, H$_2$O$_2$ did not adsorb on the two neighboring Pt atoms in the Pt-segregation region of the Pt$_1$Ag$_1$ NP and did not dissociate at various adsorption energies (Fig. 4f–h), which was also supported by the MD simulation Movie S4† (dissociation does not occur within the simulation times). Thus, we found that the alloyed Ag atoms act as a site-blocking spectator element to limit the diffusion/adsorption of H$_2$O$_2$ molecules toward/on the nearest neighboring Pt atom, thereby preventing its eventual reduction to H$_2$O. We also found that the PDR activities are strongly suppressed by Ag alloying (Pt–Ag alloy catalysts), and the PDR reaction causes the Pt catalyst to suffer a steep drop in H$_2$O$_2$ concentration with time.

The mesoscopic effects: discussion on the mass transfer perspective

In the discussion presented above, we have thus far focused on the microscopic effects under ideal conditions that influence H$_2$O$_2$ production. However, the selectivity depends not only on the surface structure but also upon the transport of H$_2$O$_2$ away from the surface in the actual device. To verify the concept of selective H$_2$O$_2$ generation in a fuel-cell system through the aforementioned active atomic sites, we characterized the relevant electrocatalytic properties employing an electrochemical H-cell and single-cell as the reactors (Fig. 5). Pt$_1$Ag$_1$/C resulted in the best H$_2$O$_2$ generation rate under 0.2 V cell voltage. Without hydrogen gas addition to the anolyte (N$_2$ purging), the counter reaction became an oxygen evolution reaction (OER), resulting in reduced H$_2$O$_2$ generation. With hydrogen gas purging, H$_2$O$_2$ generation was enhanced by the hydrogen oxidation reaction (HOR) at the anode. The H$_2$O$_2$ accumulation with the HOR counter reaction was 236.25 mol h$^{-1}$ kg$_{Pt}$m$^{-1}$. 

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Fig. 3 Proposed ORR mechanism on the Pt and Pt–Ag alloy subnanoparticles. Attachment of O–O molecule to (a) Pt, (b) segregated Pt site of Pt–Ag alloy, and (c) Pt–Ag site of Pt–Ag alloy. Attachment of H$^+$ to O–O molecule adsorbed on (d) Pt, (e) segregated Pt site of Pt–Ag alloy, and (f) Pt–Ag site of Pt–Ag alloy.

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(PDR, 2H$_2$O$_2$(aq) $\rightarrow$ 2H$_2$O + O$_2$(g)). In general, the sequential decomposition of H$_2$O$_2$ on the surface of Pt is very fast. Therefore, reducing the adverse reaction greatly affects the yield of H$_2$O$_2$ in aqueous solution. To rule out a possible artifact origin of the high H$_2$O$_2$ yield on Pt–Ag alloy, we verified suppression of the PRR and PDR through an analysis employing a 10 mM H$_2$O$_2$ solution. As shown in Fig. 4a, the Pt–Ag alloy catalysts exhibit significantly lower currents and onset potentials for the PRR relative to the Pt catalyst. Furthermore, while the Pt catalyst induced a rapid drop in the H$_2$O$_2$ concentration when 10 mg catalyst was in the solution, the PDR activity was inhibited on the Pt–Ag alloy catalysts (Fig. 4b). For the rapid dissociation of H$_2$O$_2$ using metal NPs, H$_2$O$_2$ should be adsorbed through both of the electrochemical/non-electrochemical steps on the NPs. To study the dissociation of H$_2$O$_2$ on the atomic scale, we calculated the adsorption behaviors of H$_2$O$_2$ on Pt and Pt$_1$Ag$_1$ (Fig. 4c–h). On the Pt-NP, H$_2$O$_2$ exothermally dissociated to two OH groups adsorbed on two adjacent Pt atoms through three steps: (1) adsorption of one oxygen atom in H$_2$O$_2$ (Fig. 4c); (2) O–O bond breaking in H$_2$O$_2$ (Fig. 4d); and (3) adsorption of dissociated OH on the neighboring atomic site (Fig. 4e). The results of the relevant MD simulation are given in Movies S2 and S3†. Each movie shows a different H$_2$O$_2$ dissociation path depending on the initial configuration in which H$_2$O$_2$ dissociated into two OH$^*$ (Movie S2†) or H$^*$ and H$_2$O (Movie S3†) as soon as H$_2$O$_2$ was bound to Pt. In contrast, H$_2$O$_2$ did not adsorb on the two neighboring Pt atoms in the Pt-segregation region of the Pt$_1$Ag$_1$ NP and did not dissociate at various adsorption energies (Fig. 4f–h), which was also supported by the MD simulation Movie S4† (dissociation does not occur within the simulation times). Thus, we found that the alloyed Ag atoms act as a site-blocking spectator element to limit the diffusion/adsorption of H$_2$O$_2$ molecules toward/on the nearest neighboring Pt atom, thereby preventing its eventual reduction to H$_2$O. We also found that the PDR activities are strongly suppressed by Ag alloying (Pt–Ag alloy catalysts), and the PDR reaction causes the Pt catalyst to suffer a steep drop in H$_2$O$_2$ concentration with time.

The mesoscopic effects: discussion on the mass transfer perspective

In the discussion presented above, we have thus far focused on the microscopic effects under ideal conditions that influence H$_2$O$_2$ production. However, the selectivity depends not only on the surface structure but also upon the transport of H$_2$O$_2$ away from the surface in the actual device. To verify the concept of selective H$_2$O$_2$ generation in a fuel-cell system through the aforementioned active atomic sites, we characterized the relevant electrocatalytic properties employing an electrochemical H-cell and single-cell as the reactors (Fig. 5). Pt$_1$Ag$_1$/C resulted in the best H$_2$O$_2$ generation rate under 0.2 V cell voltage. Without hydrogen gas addition to the anolyte (N$_2$ purging), the counter reaction became an oxygen evolution reaction (OER), resulting in reduced H$_2$O$_2$ generation. With hydrogen gas purging, H$_2$O$_2$ generation was enhanced by the hydrogen oxidation reaction (HOR) at the anode. The H$_2$O$_2$ accumulation with the HOR counter reaction was 236.25 mol h$^{-1}$ kg$_{Pt}$m$^{-1}$.
which was superior to that obtained with the OER counter reaction (39.22 mol h⁻¹ kg⁻¹). In total, the concentration of H₂O₂ produced on the Pt₁Ag₁/C with the OER counter reaction was 40.12 ppm in the catholyte (10 mL) during a 2 hour operation cycle; the concentration reached 240.97 ppm with the HOR counter reaction. The catalytic performance of Pt₁Ag₁/C and other catalysts was stable, as confirmed by the repeated 1 hour operation cycles (Fig. 5b, d and S11†). HAADF-STEM images of Pt₁Ag₁/C after the operation cycle indicated that most of the subnanometer/atomically dispersed elements persisted until the end of the operation (Fig. S12 and S13†). Furthermore, only little structural change of Pt–Ag alloy particles occurred (Fig. S14†). One of the important factors in determining stability is dissolution rate of Pt and Ag. We confirmed the dissolution rate by in situ/operando ICP analyses. As shown in Fig. S15a-c,† the dissolution signal of Pt and Ag wasn’t detected in ICP-OES analysis due to its low resolution. Therefore, the dissolution rates were observed through ICP-MS for more accurate analysis. The dissolution rate of Ag and Pt, confirmed by ICP-MS, were around 0.1 ppb s⁻¹ (100 ng L⁻¹ s⁻¹), respectively (Fig. S15d†). In addition, the dissolution rate of Ag decreased significantly at pH 3 (Fig. S16†). In conclusion, since the dissolution rate of Ag and Pt is too low, the activity and morphology were maintained during operation time (total reaction time = 6 h) in pH 3 solution.

According to previous studies, the MEA single-cell has poor mass transfer conditions for H₂O₂ compared to the half-cell. Under the conditions of poor mass transport, H₂O₂ has a prolonged residence time near the electrode, which accelerates its re-adsorption and subsequent conversion to H₂O. There are reports of similar mesoscopic phenomena on other catalysts, in particular, Fe–N/C. Therefore, we observed H₂O₂ production and compared its faradaic efficiencies using a single-cell with improved mass transfer. As expected, the electrolyte flow on the
catalyst surface induced a significant increase in the H$_2$O$_2$ yield (Fig. S17,† cross-sectional schematic diagram of renovated single-cell). As shown in Fig. 5e, the H$_2$O$_2$ accumulation in the renovated single-cell was 337.315 mol h$^{-1}$ kg$_{M}$, which was much higher than that of the H-cell (236.25 mol h$^{-1}$ kg$_{M}$). In the single-cell, the oxygen gas was in direct contact with the catalyst surface, so the activity significantly increased. However, due to the low solubility of oxygen gas in water-based electrolytes, a relatively small amount of oxygen was in contact with the catalyst surface in the H-cell structure.

The H$_2$O$_2$ faradaic efficiencies for H-cells and single-cells were calculated from the H$_2$O$_2$ yields against the quantity of charge passed:

$$\text{H}_2\text{O}_2 \text{ faradaic efficiency (\%)} = \frac{2CVF}{Q}$$

where C is the H$_2$O$_2$ concentration (mol L$^{-1}$), V is the volume of electrolyte (L), F is the Faraday constant (96 500 C mol$^{-1}$), and Q is the amount of charge passed (C). Fig. 5f shows the faradaic efficiencies of the H-cell and single-cell experiments. Pt$_{1}$Ag$_{1}$/C catalyst exhibit comparable and superior activity and selectivity in the H-cell and single-cell to the best known electrocatalysts for H$_2$O$_2$ production (Table S3†). The peculiar point is that the faradaic efficiency and H$_2$O$_2$ production in single-cells are higher than those of H-cells. This difference is attributed to the proton diffusion and electrolyte flow between the membrane and the catalyst layer. We improved proton diffusion by adopting Nafion beads, but the diffusion is still insufficient.

**Fig. 5** The accumulated H$_2$O$_2$ concentrations for the prepared catalysts in a H-cell with (a) the OER and (c) HOR counter reactions using a Nafion 212 membrane. The reported catalytic performance for H$_2$O$_2$ production with HOR in an H-cell is shown in (c). Accumulated concentrations of H$_2$O$_2$ produced on the Pt$_{1}$Ag$_{1}$/C catalyst with the (b) OER and (d) HOR counter reactions during repeated 1 hour operation cycles. (e) The accumulated H$_2$O$_2$ concentrations for the prepared catalysts in the renovated single-cell with the HOR counter reaction. (f) Faradaic efficiency of H$_2$O$_2$ production for the H-cell and the single-cell. The reported results are also shown in the (f).
oxidation process that enables the spot utilization of \( \text{H}_2\text{O}_2 \).

We proposed appropriate conditions for \( \text{H}_2\text{O}_2 \) production in a real device through a renovated single-cell experiment in which (1) electrolyte flow was supplied between the membrane and the cathode to improve the diffusion of \( \text{H}_2\text{O}_2 \), (2) the proton diffusion was improved by adopting Nafion beads in the electrolyte flow channel, and (3) the direct contact of oxygen molecules with the catalyst surface was increased. We propose that further improvement in the proton diffusion to the level of that in the general MEA single-cell and adopting a more hydrophobic cathode material will yield better \( \text{H}_2\text{O}_2 \) production performance.

Electro-Fenton process: organic pollutant removal. Adopting \( \text{H}_2\text{O}_2 \) generation using the Pt–Ag alloy catalyst, we degraded organic toxins adopting an electro-Fenton process, and we assessed the reaction kinetics. An electro-Fenton process is a cost-effective, eco-friendly electrochemical advanced-oxidation process that enables the \textit{in situ} generation and on-the-spot utilization of \( \text{H}_2\text{O}_2 \).\textsuperscript{50,51} The target toxins were microcystin (MC)-LR and MC-RR, which are well known to be generated by cyanobacteria species. These toxins are often classified as hepatotoxins (MC-LR, RR),\textsuperscript{52} and the intraperitoneal LD\textsubscript{50} for mice is 36–122 \( \mu \text{g \text{kg}^{-1}} \) (MC-LR)\textsuperscript{53} and 235 \( \mu \text{g \text{kg}^{-1}} \) (MC-RR).\textsuperscript{54}

Fig. 6a shows the degradation profiles for MC-LR and MC-RR plotted against the electro-Fenton reaction times. The results show that 94.2% of MC-LR and 96.2% MC-RR were eliminated after 60 min, despite the excess initial concentrations (5 mg L\textsuperscript{-1}) under ORR operation conditions. The corresponding rate constant (\( k \)) can be calculated by considering the pseudo first-order kinetic model and fitting the normalized concentration vs. time profiles for MC degradation. The rate constants and the statistical correlation parameters are shown in Fig. 6b. As expected from the concentration–time profile, the kinetic parameter values were \( k = 0.1195 \text{ min}^{-1} \) and 0.0786 min\textsuperscript{-1} for MC-LR and MC-RR, respectively. The results indicate that \( \text{H}_2\text{O}_2 \), electro-generated from the ORR on the Pt–Ag alloy cathode, can be effectively utilized as a reactant for an electro-Fenton process.

**Conclusions**

We synthesized Pt–Ag alloy catalysts, which exhibited subnanometer-scale particle size and atomic scale dispersion of alloying elements. Its ORR behavior significantly differed from that of a Pt catalyst due to Ag atoms with poor oxygen adsorption. The present Pt–Ag alloy nanoparticles selectively catalyzed the two-electron ORR pathway rather than the four-electron ORR counterpart. Consequently, the present Pt–Ag alloy nano-catalyst serves as a powerful and convenient route for \( \text{H}_2\text{O}_2 \) production in electric power generation through fuel-cell systems, which enables the direct removal of various organic pollutants in synthetic and actual wastewater. Finally, it is important to acknowledge that superior performance in an RRDE does not necessarily lead to superior performance in a real device. As a result of our efforts to resolve this issue, we confirmed that improving the diffusion of \( \text{H}_2\text{O}_2 \) could result in a faradaic efficiency similar to that observed in the RRDE experiment.

Hydrogen peroxide is a nontoxic and versatile commodity chemical. Environmental concerns and the consequent legislation indicate strongly increased demand for \( \text{H}_2\text{O}_2 \) over the coming years. In particular, we emphasize that most applications require \( \text{H}_2\text{O}_2 \) to act upon the effluents in water. The direct electrochemical production of \( \text{H}_2\text{O}_2 \) using a stable, efficient catalyst is especially attractive for this purpose. The conclusions section should come in this section at the end of the article, before the acknowledgements.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


