Recent Progress in Nanoparticle Synthesis via Liquid Medium Sputtering and its Applications

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ABSTRACT

Nanoparticles (NPs), which have been investigated intensively as electrocatalysts, are usually synthesized by chemical methods that allow precise size and shape control. However, it is difficult to control the components and compositions of alloy NPs. On the other hand, the conventional physical method, sputtering with solid substrates, allows for facile composition control but size control is difficult. Recently, “liquid medium sputtering” has been suggested as an alternative method that is capable of combining the advantages of the chemical and conventional physical methods. In this review, we will discuss NP synthesis via the liquid medium sputtering technique using ionic liquid and low-volatile polymer media. In addition, potential applications of the technique, including the generation of oxygen reduction reaction electrocatalysts, will be discussed.

Keywords : Sputtering, Ionic liquid, Low-volatile polymer, Nanoparticle, Oxygen reduction reaction.

Received November 22, 2015 : Revised November 2, 2015 : Accepted November 3, 2015

1. Introduction

The oxygen reduction reaction (ORR), in which a strong O-O bond (498 kJ/mol) is broken, is very sluggish—for example, in a proton exchange membrane fuel cell (PEMFC), the overpotential of the ORR at the cathode is generally very high (500–600 mV), whereas that of the hydrogen oxidation anode is low (50 mV) [1]. For this reason, highly active Pt and Pt-based materials are conventionally utilized as ORR electrocatalysts in electrochemical systems such as PEMFCs and metal-air batteries [2]. Using Pt significantly increases material costs; thus, decreasing the amount of Pt in PEMFCs is an important technical target. Since only surface atoms can catalyze electrochemical reactions, including the ORR, a high fraction of surface atoms is desirable to achieve efficient

utilization of expensive Pt. For example, in Pt nanoparticles (NPs) with diameters of 3 nm, around 50 % of Pt atoms exist on the surface and are used as ORR active sites [3]. Moreover, in NPs, quantum effects can change or enhance properties such as reactivity, strength, and electrical characteristics [4]. Besides the ORR, NPs can catalyze many electrochemical reactions, including the hydrogen evolution [5,6], liquid fuel (e.g., methanol [7,8], ethanol [9,10] and formic acid [11,12]) oxidation, and carbon dioxide reduction reactions [13].

NPs can be fabricated by both “bottom-up” and “top-down” approaches, which utilize solution-phase colloidal chemistry (the chemical method) and conventional physical methods on solid substrates, respectively [14]. The chemical method allows for synthesis of uniform NPs, the size and shape of which can be

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Open Access DOI: <http://dx.doi.org/10.5229/JECST.2016.7.1.19>

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controlled by varying the reaction conditions. However, fabrication of alloy NPs with defined compositions is difficult, and it is hard to control the final alloy composition [15]. Other disadvantages of the chemical method include the requirement of additives (reducing agents and surfactants) and the formation of byproducts. In contrast, the use of conventional physical methods on solid substrates, based on direct atomization of metals in vacuum using techniques such as thermal evaporation or sputtering, allows for greater flexibility in the choice of materials and compositions. Moreover, it is an environmentally friendly technique, as no additives and byproducts are involved. However, size control is very difficult in conventional physical methods, as they are based on film formation processes. In order to increase control over the NP formation process, several strategies have been developed [16-18]. For example, in a work by Masini and coworkers, the deposition was separated from particle condensation, and a time-of-flight mass filter was inserted between the two sections [16]. Despite improved uniformity and size control, the use of complex apparatus makes broad application of this modified top-down approach unviable.

As an alternative to these methods, "liquid medium sputtering" has recently attracted considerable attention. In this technique, liquid substrates with extremely low vapor pressures, such as ionic liquids (IL) and non-volatile polymers, are used to fabricate NPs by sputtering. Scheme 1 shows the schematic illustration of liquid medium sputtering. Apart from using a liquid as a substitute for a normal solid substrate, the apparatus is identical to general sputtering

equipment. A non-volatile liquid containing vessel is placed on a sample holder, where the solid substrate for film deposition should be positioned in common sputtering systems. During sputtering, particles that are ejected from the target material diffuse within the liquid medium and form a colloidal solution. Since the ejected nanosized metal particles are dispersed in a liquid medium in a colloidal solution state, uniformity and tunability in the composition can be achieved simultaneously. Using this technique, uniformly dispersed 1.9 nm and 5.5 nm Au NPs have been prepared in two different ILs via a clean and simple route by Torimoto and co-workers [19]. It is promising that the limitations of the conventional physical methods, viz., poor size distribution and control, could be overcome while retaining their advantages. The following works explore various metals and low volatility liquids as potential NP materials and liquid substrates, respectively.

In this review, we summarize recent progress in NP synthesis via liquid medium sputtering and its potential applications, which includes the generation of electrocatalysts for ORR. First, metal NP synthesis using ionic liquids will be discussed, which includes the synthesis of single material NPs and the effect of sputtering conditions [19-27], various alloying strategies [15,23,24,28], and techniques for transferring synthesized NPs [29-31]. Subsequently, we discuss NP synthesis using low-volatile polymers, including the use of thiol compounds and transfer techniques [32-39]. Finally, potential applications of liquid medium sputtered NPs, such as their use as ORR electrocatalysts and Suzuki-Miyaura coupling reac-

Scheme. 1. Left: a schematic illustration of liquid medium sputtering. Right: colloidal solution product of liquid medium sputtering.

tion catalysts, will be introduced [25,30,35,39-41].

2. Liquid medium sputtering onto ionic liquids

2.1 Single material NP synthesis

In 2006, the first paper using liquid sputtering for nanoparticle synthesis was published [19]. Sputtering deposition of gold was carried out with a 4.0 mA current under a 20 Pa air atmosphere without the use of additional chemical species (such as reducing and/or stabilizing agents). Two ionic liquids, N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄), were selected as liquid substrates. Highly stable and uniform nanoparticles were obtained despite the absence of any additional stabilizing agents, and the particle size was dependent on the type of IL used. The Au NPs in EMI-BF₄ had an average diameter of 5.5 nm with a standard deviation of 0.86 nm, while Au NPs in TMPA-TFSI had an average diameter of 1.9 nm and a standard deviation of 0.46 nm (Fig. 1).

Following on from this initial work, the effects of the Au NP deposition conditions were investigated. For example, Hatakeyama et al. studied the effect of the IL substrate temperature [20]. For this analysis, they remodeled the sputtering coater by attaching a device for circulating temperature-regulated water into the base of the deposition target. Gold foil sputtering was conducted at a voltage of 1 kV, a current of 20 mA under a 12-13 Pa Ar atmosphere, and at constant temperatures between 20 °C and 80 °C. The capture medium used was 1-buthyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄). Particle size was relatively uniform, as detected by small-angle X-ray scattering (SAXS) measurements, and the size was strongly dependent on the temperature of the IL. The authors suggested that modulation of the temperature caused changes in the viscosity of the liquid, and therefore the diffusive velocities of the scattered Au particles. Variation of particle size with temperature can be seen in Fig. 2.

Hatakeyama et al. also studied the effect of altering various other sputtering conditions on Au NP synthesis [21]. BMI-BF₄ and gold foil were used for sputtering, and the target-to-substrate distance was between 25 and 75 mm. The applied voltage and discharge current were varied in the ranges of 700-1000 V and 20-40 mA, respectively. The results revealed that both the temperature of the target and

the voltage applied had a strong influence on the size of the Au NPs generated in the capture media, while the working distance between the target and the surface of the capture media, the sputtering time, and the

Fig. 1. Transmission electron microscopy (TEM) images of Au NPs prepared by sputter deposition onto (a) EMI-BF₄ and (b) TMPA-TFSI. Reprinted with permission from Ref. [19]. Copyright [2006], AIP Publishing LLC.

Fig. 2. Temperature dependencies of sputter deposited Au NP size vs. diameter of peak-top (d_{peak}) and full width at half maximum (W_{FWHM}). The sizes of the cuboctahedrons with closed-shell structures are illustrated by the broken lines on the left. Reprinted with permission from Ref. [20]. Copyright (2010) American Chemical Society.

discharge current had little or no influence. Fig. 3 (re-dited from ref. [21]) shows the effect of each factor. From this information, the authors concluded that size control was possible with a lower target temperature and higher applied voltage, yielding smaller NPs.

The growth of Au NPs after sputtering into 1-butyl-3-methylimidazolium dicyanamide (BMI-N(CN)₂), 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆), 1-butyl-3-methylimidazolium triflate (BMI-TfO), BMI-TFSI, and BMI-BF₄ was studied by Vanecht and coworkers [22]. The sputtering experiments were performed under argon at a pressure of 0.1 mbar, an electric current of 50 mA, a sputter time of 60 s, and a target-substrate distance of

40 mm with a gold target. The authors found that primary NPs with diameters under 2.5 nm were present in the sample immediately after sputtering, and that the NPs grew after the termination of the sputtering process, stopping when they reached a certain size. The work also revealed that particle growth was strongly dependent on the viscosity of the IL. The growth was fastest in the least viscous IL and followed the trend BMI-N(CN)₂ > BMI-TFSI > BMI-TfO > BMI-BF₄ > BMI-PF₆, as shown in Figs. 4 and 5.

In addition to Au, various other metal NPs have been fabricated by sputtering onto ionic liquids, including Pt [23], Ag [24], and Pd NPs for Suzuki-Miyaura coupling reactions [25], transition metal

Fig. 3. (a) The sputtering-time dependencies of the sputter deposited Au NP size based on d_{peak} (closed symbols) and W_{FWHM} (open symbols) at 20 °C (blue squares) and 50 °C (red circles). (b) The size distributions of Au NPs synthesized under different currents (20, 30, and 40 mA) at fixed voltages of either 700 or 1000 V. The d_{peak} (closed circles) and W_{FWHM} (open circles) values vs. the discharge current are illustrated in the inset. (c) The particle size distributions vs. diameter for the scattering profiles. The working distance dependencies of d_{peak} (closed circles) and W_{FWHM} (open circles) are shown in the inset. Reproduced from Ref. [21] with permission from The Royal Society of Chemistry.

Fig. 4. Representative TEM images of Au NPs in the ionic liquid, BMI-N(CN)₂, sampled from the bulk ionic liquid (a) 1 min after sputtering, (b) 2 h after sputtering, (c) 6 h after sputtering, and (d) 24 h after sputtering, with the corresponding histograms of the size-distribution of Au NPs shown below. Reproduced from Ref. [22] with permission from the PCCP Owner Societies.

NPs (W, Mo, Nb, Ti) [26], and hollow indium oxide NPs using the Kirkendall effect [27].

2.2 Alloy NP synthesis

Several researchers have attempted to extend the scope of sputter deposition on ionic liquids beyond single material NPs by using the technique to synthesize alloy NPs. Three different strategies have been adopted for alloy NP synthesis: 1) preparation of fan-shaped targets with separate areas of each metal, 2) dissolution of a counter-metal precursor in the liquid substrate, and 3) co-sputtering of two different targets.

Okazaki et al. used the first strategy in their

research for the single-step synthesis of gold-silver alloy NPs [24]. The authors selected BMI-PF₄ as the sputtering medium and prepared a target composed of radially arranged Au and Ag foils (Fig. 6). Sputter deposition was carried out for 300 s using a current of 40 mA under a 20 Pa Ar atmosphere at room temperature. The authors showed that the peak wavelength red-shifted when the proportion of gold foil on the target was increased. This was evidence of alloy formation, because Au-Ag bimetallic alloy nanoparticles exhibit a composition-dependent surface plasmon resonance (Figs. 7 and 8).

Suzuki et al. also applied an analogous strategy to fabricate AuPt bimetallic NPs dispersed in TMAPA-TFSA at room temperature [23]. In this paper, alloy

Fig. 5. Peak absorbance as a function of time after sputtering in different ionic liquids: BMI-N(CN)₂, BMI-TFSI (Tf₂N), BMI-TfO, BMI-BF₄, and BMI-PF₆. Reproduced from Ref. [22] with permission from the PCCP Owner Societies.

Fig. 6. (a) Schematic illustrations of Au-Ag foil binary targets having various fractions of Au (f_{Au}). (b) Photographs of BMI-PF₆ obtained after sputter deposition of Ag ($f_{Au} = 0$, left), Au-Ag ($f_{Au} = 0.50$, center), and Au ($f_{Au} = 1$, right) nanoparticles. Reproduced from Ref. [24] with permission from The Royal Society of Chemistry.

Fig. 7. (a) TEM images and (b) size distributions of Au-Ag alloy NPs obtained by sputter deposition onto BMI-PF₆ with $f_{Au} = 0, 0.50$, and 1.0 . The bars in the figures represent a length of 5 nm. Reproduced from Ref. [24] with permission from The Royal Society of Chemistry.

formation was detected more directly using X-ray Diffraction (XRD) after collecting the NPs by centrifugation. The activity for methanol oxidation was also demonstrated for AuPt NPs, which were immobilized on a highly ordered pyrolytic graphic (HOPG) substrate, by cyclic voltammetry (CV) measurements.

The second strategy has been used to synthesize AuAg alloy NPs using a chemical reaction induced by sputter deposition of Ag onto IL solutions containing HAuCl_4 [28]. A red-shift in the surface plasmon

Fig. 8. Normalized absorption spectra of BMI- PF_6 after the simultaneous sputter deposition of Au and Ag with (i) $f_{\text{Au}} = 0$, (ii) 0.25, (iii) 0.50, (iv) 0.75, and (v) 1.0. The arrows show the surface plasmon resonance (SPR) band peak. (Inset) The dependence of the peak wavelength of the SPR band (λ_{SPR}) on f_{Au} . Reproduced from Ref. [24] with permission from The Royal Society of Chemistry.

resonance peak in the absorption spectra was detected when the concentration of HAuCl_4 was increased, indicating that AuAg alloy NPs were synthesized, similarly to the previously mentioned AuAg NPs.

AuCu NPs were obtained via the last strategy, referred to as the co-sputtering technique [15]. The combinatorial fabrication of alloy NPs was performed by co-sputtering from two elemental targets (Cu and Au) positioned opposite to each other (Fig. 9). BMI-TFSI was placed in a micro-machined cavity array substrate, and the relative content of the metals was altered by positioning the substrate closer to the material that is desired in a higher proportion. Co-sputtering was conducted at a pressure of 5 mTorr and under a constant Ar gas flow of 40 sccm. The obtained NPs were smaller than 7 nm and had narrow size distributions, especially the pure elemental particles. The size and shape of the NPs changed with their composition (see Fig. 10).

2.3 Transfer of NPs

Before NPs can be utilized, they must first be rearranged into a controllable phase. Immobilization onto organized surfaces or levigation of the NPs through precipitation processes have both been used for this purpose.

Khatri et al. demonstrated the interaction of BMI- PF_6 -stabilized Au NPs with a (3-mercaptopropyl)trimethoxysilane (MPS)-functionalized silicon surface [29]. The BMI- PF_6 supramolecular aggregates coordinate loosely to Au NPs and could be replaced with thiol molecules. However, the density -number of immobilized particles per unit area- was relatively low. This led the same research group to investigate a new process for immobilizing sputter deposited Au

Fig. 9. Left: Schematic (not to scale) of combinatorial co-deposition from two sputter targets into a cavity array substrate filled with IL. Right: Schematic of the proposed formation process of NPs in IL. Reproduced from Ref. [15] by permission of John Wiley & Sons Ltd.

Fig. 10. TEM bright-field images of (a) Cu NPs, (b) Au NPs, and (c)-(e) Au-Cu alloy NPs with different chemical compositions show that the changes in size and shape of the NPs vary with different compositions. All were precipitated and capped with organic surfactants. A representative NP size distribution is shown in (f). The red line in (f) represents a fit to the data. Reproduced from Ref. [15] by permission of John Wiley & Sons Ltd.

NPs on HOPG via thermally induced self-assembly [30]. Gold NP-containing room temperature ionic liquid (RTIL) solutions were dropped onto the HOPG surface, which then underwent heat treatment under vacuum. The Au-immobilized HOPG surface was washed with acetonitrile several times and then analyzed. The TEM images in Fig. 11 show that Au NPs were successfully immobilized on the HOPG surface, and that their size could be controlled by varying the temperature without using additional stabilizing agents

such as thiol compounds. The immobilized films were also stable during electrochemical measurements.

Suzuki et al. proposed a novel strategy for controlling the adsorption positions of NPs on solid substrates by varying the electrostatic interactions between the substrate surface and the ILs, by using a rutile TiO₂ (110) single crystal surface and Au NPs obtained from liquid medium sputtering [31]. The authors revealed that the combination of a charged surface and charged molecules had the potential to

afford control of the NP location on the surface, by tuning the electrostatic interactions. Fig. 12 illustrates how the adsorption of the NPs on TiO_2 varied with

Fig. 11. AFM images of Au-immobilized on a HOPG surface. HOPG was treated with Au sputter-deposited TMPA-TFSA (a) without and (b) with heating at 373 K and (c) 423 K. A sample for image (d) was obtained by treating HOPG with Au-deposited BMI- PF_6 at 423 K. Reproduced from Ref. [30] by permission of CSJ Publications.

the use of different ILs.

A precipitation protocol that showed no agglomeration or significant growth of NPs was developed by König and co-workers [15]. Gold, copper, and AuCu alloy NPs dispersed in BMI-TFSI were completely dissolved in acetonitrile that contained only a small amount of organic surfactants (1-hexadecylamine (HDA) and/or 1-dodecanethiol (DCT)). After the mixture became turbid and flocculation occurred, the precipitate was centrifuged and washed several times with acetonitrile, then centrifuged again for 10 min at 2000 rpm. A postulated precipitation mechanism is depicted in Fig. 13.

Fig. 13. Postulated precipitation mechanism of Cu NPs from the IL/acetonitrile mixture after addition of hexadecylamine. Reproduced from Ref. [15] by permission of John Wiley & Sons Ltd.

Fig. 12. Typical AFM images of TiO_2 (110) surfaces treated with the ILs of (a) $\text{C}_4\text{MIm-BF}_4$, (b) $\text{C}_4\text{MIm-NTf}_2$, (c) $\text{C}_4\text{MIm-PF}_6$, (d) PY1,10I1-BF_4 , and (e) N122,10I2-BF_4 , followed by immobilization by heating at 323 K. Reproduced from Ref. [31] with permission from the PCCP Owner Societies.

3. Liquid medium sputtering onto low-volatile polymers

3.1 C-H-O-containing polymers

Although sputter deposition onto ILs is a clean and facile method for synthesizing uniform NPs, the high cost of ILs is an obstacle for their use in various applications. Several researchers have suggested using low-volatile liquid polymers as an alternative. Polyethylene glycol (PEG), which is economical, environmentally friendly, and biocompatible, is the most widely investigated potential candidate.

Hatakeyama et al. used PEG with an average molecular weight of 600 as a sputtering medium, because it is in the liquid state at room temperature and has a vapor pressure low enough to endure the sputtering process [32]. The deposition was performed at a voltage of 1 kV, a current of 20 mA under an Ar pressure of 16-19 Pa, and at constant temperatures of 20, 30, 40, 50, and 60 °C. Although Au NPs were successfully synthesized in PEG, the size and size distribution of the Au NPs were larger and wider, than those of Au NPs in BMI-BF₄, as illustrated in Fig. 14. The authors explained that the stabilization capability of PEG seemed to be weaker than that of BMI-BF₄, as there is no coordination by anions and/or cations around the NPs in PEG. In the same man-

ner, Au NPs in PEG were more strongly affected by changes in temperature, as illustrated in Fig. 15. However, it is clear that the use of PEG allows for the preparation of Au NPs by a simple, facile, and inexpensive process.

Wender et al. used castor oil, a biocompatible low-volatile fluid that is composed mainly of a mixture of triglycerides predominantly derived from unsaturated and hydroxylated fatty acids, as a liquid sputtering medium for Au NP synthesis [33]. Sputter deposition of the Au target at 330 V for 300 s yielded Au NPs with diameters of 3.6 ± 1.0 nm. The researchers also investigated the effect of discharge voltage on particle size, and found that increased sputtering energy caused a significant increase in the diameter of the NPs.

In addition to PEG and castor oil, canola oil [34], caprylic/capric triglyceride (CCT) oil [34], pentaerythritol ethoxylate (PEEL) [35], and propane-1,2,3-triol [36] have been successfully used as sputtering media for NP synthesis.

3.2 Introduction of thiol functional groups

PEG is a weaker NP stabilizer than ILs due to the absence of anion and/or cation coordination, which results in poorer size control and higher sensitivity to temperature changes. Ishida et al. used a thiol stabilizer to enhance the stabilization ability of PEG. Ag was sputtered onto PEG containing $0, 5.2 \times 10^{-4}, 2.6 \times 10^{-3}$,

Fig. 14. (a) Colors of Au NPs in PEG prepared at 20 °C and 60 °C. Both solutions were diluted with PEG from an initial concentration of about $40 \text{ mmol} \cdot \text{dm}^{-3}$ by a factor of 100. TEM images of Au NPs prepared by sputter deposition into liquid PEG at (b) 20 °C and (c) 60 °C. Reprinted with permission from Ref. [32]. Copyright (2011) American Chemical Society.

Fig. 15. T/η dependencies of d_{peak} (closed marks) and W_{fwhm} (open marks) for Au NPs in PEG (red circles) and Au NPs in BMI-BF₄ (blue squares). Reprinted with permission from Ref. [32]. Copyright (2011) American Chemical Society.

Fig. 16. TEM images and size-distribution histograms of Ag NPs prepared at MUA concentrations of (a) 0, (b) 5.2×10^{-3} , and (c) 5.2×10^{-1} M in PEG. The inset shows the expansion of the histograms. (d) Average diameter of Ag NPs prepared at various MUA concentrations from 0 to 5.2×10^{-1} M. The inset shows the expansion plots from 0 to 0.007 M. Reproduced from Ref. [37] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Fig. 17. (a) High angle annular dark field STEM image of Ag NPs prepared using a 5.2×10^{-1} M concentration of MUA in PEG. EDX mapping images of (b) Ag, (c) S, and (d) Ag + S. The green square in image (a) represents the area used for EDX mapping for (b)-(d). Reproduced from Ref. [37] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

5.2×10^{-3} , 5.2×10^{-2} , and 5.2×10^{-1} M of 11-mercaptopundecanoic acid (MUA) using a current of 30 mA under Ar at a pressure of 2.0 Pa [37]. Altering the concentration of MUA in PEG afforded direct control of the size of resulting Ag NPs, with particles ranging from 2.2 to 7.4 nm in diameter (Fig. 16). According to the energy-dispersive X-ray spectroscopy (EDX) mapping image in Fig. 17, the S atoms are concentrated on the surface of the Ag NPs, and the scanning transmission electron microscopy (STEM) images clearly indicate stabilization of the Ag NPs by MUA.

In addition to thiol additives, thiol-containing polymers such as (6-mercaptohexyl)trimethylammonium bromide (6-MTAB) [38] and pentaerythritol tetrakis-(3-mercaptopropionate) (PEMP) [35] have been used

as sputtering media. Au NPs were synthesized in both reports, and the Au NPs with PEMP produced smaller particles than those with 6-MTAB. This was due to the four -SH groups per molecule of PEMP, which results in more rapid protection of sputtered Au atoms by PEMP than 6-MTAB, which has only one -SH group per molecule.

3.3 Transfer of NPs

As mentioned in Section 2.3, NP transfer without shape deformation is required for successful utilization of synthesized NPs. Immobilization of NPs in PEG on carbon supports was reported by Cha and co-workers [39]. Platinum and PtNi alloy NPs, with sizes of approximately 2 nm, were uniformly deposited via

direct sputtering onto a dispersed carbon support containing PEG as a medium. As a result, carbon-supported Pt or PtNi NP powders (Pt/C or PtNi/C) were easily obtained via filtration of the as-prepared solutions. No additives or heat treatment was required for immobilization of the NPs on the supports, in contrast to NPs in ILs. Fig. 18 shows transmission electron microscopy (TEM) images of NPs on carbon supports.

4. Application of sputter deposited NPs

4.1 ORR electrocatalysts

Electrochemical activities of liquid medium sputtering deposited NPs for ORR have been examined by a few research groups. Okazaki et al. presented cyclic voltammograms (Fig. 19) of various electrodes in an O_2 -saturated $0.5 \text{ mol}\cdot\text{dm}^{-3}$ aqueous KOH solution [30]. Though a bare HOPG electrode showed no peaks, quasi-reversible redox peaks were observed when a gold nanoparticle-immobilized HOPG electrode was used; a cathodic peak appeared near the range of -0.30 – -0.35 V due to the two-electron reduction of O_2 to form HO_2^- , and an anodic peak appeared at 0.05 V owing to the oxidation of HO_2^- .

A Pt-embedded glassy carbon electrode (Pt-GCE) consisting of a Pt-sputtered RTIL and a glassy carbon plate exhibited favorable catalysis for ORR [40]. Platinum NPs were prepared in trimethyl-*n*-propylammonium bis((trifluoromethyl)sulfonyl)amide ($\text{Me}_3\text{PrN-Tf}_2\text{N}$) with a sputter current of 40 mA in a dry Ar (99.999 %) atmosphere. After heat treatment for immobilization, the glassy carbon plates were either immersed in a 1.67 M solution of KOH in isopropanol for 12 h or rinsed with dry acetonitrile. The catalytic activity of these Pt-GCEs in an O_2 -saturated H_2SO_4 aqueous solution was examined by CV. The observed current densities were based on the active surface area of the Pt nanoparticles. In each case, a distinct reduction wave for the ORR appeared.

Synthesis of electrochemically active carbon-supported NPs was also achieved via direct one-step sputtering onto a carbon-containing liquid substrate by Cha and co-workers [39]. Pt and PtNi alloy NPs on carbon supports were obtained via either direct Pt sputtering or Pt and Ni co-sputtering onto carbon supports dispersed in a PEG solution, followed by filtration of the as-prepared solutions. No additives or heat treatments were required for immobilization of the NPs on the supports. Electrochemical tests were conducted in 0.1 M

Fig. 18. TEM images of (a) Pt/C and (b) PtNi/C. Insets (a) and (b) show magnified high-resolution TEM images (upper) and nanoparticle size distribution (lower). Reproduced from Ref. [39] with permission from The Royal Society of Chemistry.

Fig. 19. Cyclic voltammograms for the ORR in O_2 -saturated aqueous KOH solution using a bare HOPG electrode (dotted line) and a Au NP-immobilized HOPG electrode (solid line). Potential scan rate: $0.10 \text{ V}\cdot\text{s}^{-1}$. Reproduced from Ref. [30] by permission of CSJ Publications.

HClO₄ at 293 K with an Ar-purged atmosphere for CV and an O₂-purged atmosphere for linear sweep voltammetry, at a rotation speed of 1600 rpm. The superior oxygen reduction activity of PtNi/C was also evaluated using electrochemical analysis, as depicted in Fig. 20.

4.2 Suzuki-Miyaura coupling reaction catalysts

Oda et al. [25] demonstrated the catalytic activity of Pd nanoparticles in BMI-PF₆ and BMI-TFSI for the Suzuki-Miyaura coupling reaction, where the coupling partners are a boronic acid with a halide. In this paper, iodobenzene and p-tolylboronic acid were used as starting materials to synthesize 4-methylbiphenyl. Pd nanoparticles in BMI-PF₆ were generated with an average diameter of 3.0 nm, whereas the use of BMI-TFSI resulted in a 2.2 nm average diameter.

Due to the insolubility of iodobenzene in water, the reaction should proceed in a biphasic system, i.e., organic particles in water. Use of i-Pr₂N⁺Et and water afforded optimal conditions for the Pd/BMI-PF₆ catalyst (70 % yield). On the other hand, in the case of Pd/BMI-TFSI, Cs₂CO₃ and water gave the maximum yield, 72 %. Suzuki-Miyaura couplings of various aryl iodides and bromides with arylboronic acids were also conducted and catalyzed efficiently by the Pd/BMI-TFSI catalyst.

4.3 Hybrid resin synthesis

Shishino et al. demonstrated that sputtering onto

Fig. 20. (a) Polarization curves for the oxygen reduction activities of Pt/C, PtNi/C, and a commercial Pt/C electrocatalyst obtained at 1600 rpm and 5 mV·s⁻¹ in an O₂-saturated 0.1 mol·L⁻¹ HClO₄ electrolyte. Inset shows mass specific activities. Reproduced from Ref. [39] with permission from The Royal Society of Chemistry.

RTIL can be used to prepare transparent inorganic/organic hybrid resins [35]. Since inorganic/organic hybrid optical materials can display material properties, such as the index of refraction or thermal, mechanical, and luminescent properties, they have garnered much interest. To obtain transparent hybrid materials that include NPs, the size of NPs in the hybrid material should be smaller than one-tenth the wavelength of visible light and NPs. Moreover, addition of a dispersing agent is required to minimize aggregation of the NPs. Therefore, the liquid medium sputtering method is appropriate for the preparation of hybrid resins.

Liquid medium sputtering of a Au target afforded AuNPs/PEMP and AuNPs/PEEL hybrids, which could be readily transformed into thiourethane and urethane resins via heat polymerization, respectively. After polymerization, highly transparent AuNPs/thiourethane and AuNPs/urethane hybrid resins were obtained (Fig. 21). This study confirms that hybrid resins with various functional properties can be prepared using liquid medium sputtering, by controlling the interaction strength between the metal surface and the matrix material.

4.4 Nanoframe synthesis

Okazaki et al. reported Au nanoframe synthesis using Ag cubes as templates [41]. Au-NPs prepared by sputter deposition of Au in an ionic liquid were selectively assembled at the edges and vertices of Ag

Fig. 21. UV/Vis transmittance spectra of urethane (orange), fresh AuNPs/urethane (green), and matured AuNPs/urethane with $t_s = 3$ min (thickness: 1.3 mm) (blue); inset: photographs of fresh (left) and aged (right) AuNPs/urethane. Reproduced from Ref. [35] by permission of John Wiley & Sons Ltd.

Fig. 22. SEM images of ODT-AMP-Ag nanocubes obtained after deposition of Au NPs. (Inset) Corresponding Au nanoframe prepared by chemical etching of Ag nanocube. The scale bar in each image represents 250 nm. Reproduced from Ref. [41] by permission of CSJ Publications.

nanocubes, the surfaces of which were modified with a self-assembled monolayer of 1-octadecanethiol (ODT) and 4-amino-2-mercaptopyrimidine (AMP). In detail, a BMI-PF₆ solution containing surface modified Ag nanocubes was mixed with a Au sputter-deposited BMI-PF₆ solution. The resulting solution was annealed at 423 K to obtain AuAg binary particles. Chemical etching of Ag from the AuAg binary nanocomposites resulted in the formation of Au nanoframes. (Fig. 22)

Both the ODT and AMP on the Ag surface directed thermally induced site selective deposition of Au NPs onto Ag nanocubes. It is expected that the present technique has much potential for the preparation of more complicated three-dimensional nanostructures that have unique plasmonic, magnetic, or catalytic properties, by the self-assembly of metal/alloy nanoparticles on Ag nanoparticles.

5. Conclusion

In this review, we have discussed NP synthesis using the liquid medium sputtering technique. The effects of medium viscosity, sputtering conditions, and temperature have been investigated using various ILs as media, and NP growth mechanisms were postulated based on these results. In addition to single metal materials, alloy NPs have been synthesized using either sectioned targets or co-sputtering. Several NP transfer techniques have been investigated in order to explore the potential utilization of as-prepared NPs.

Nanoparticles have been immobilized on highly ordered substrates through the heat treatment or introduction of thiol functional groups, and precipitating without size increment has been shown to be possible after a specific additive-induced precipitation process.

Several low-volatile and economical liquid polymers have been proposed as substitutes for expensive ILs, and it was found that NPs can also be obtained using polymeric media. Thiol functional groups have been introduced to polymers to enhance the size control of polymeric media, which is limited due to their lack of anion and/or cation coordination.

The NPs synthesized displayed electrocatalytic activity for ORR, and supported NPs prepared via one-step sputtering onto carbon supports containing PEG exhibited superior oxygen reduction activities over commercial electrocatalysts. Moreover, liquid medium sputtering could be applied to yield Suzuki-Miyaura coupling reaction catalysts for the fabrication of hybrid resins or nanoframes.

Acknowledgements

This study was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20133030011320, No. 20143010031770, and No. 20153010041750).

References

- [1] A. A. Gewirth and M. S. Thorum, *Inorg. chem.*, **49**(8), 3557 (2010).
- [2] O. T. Holton and J. W. Stevenson, *Platinum Metals Review*, **57**(4), 259 (2013).
- [3] N. Taniguchi, *On the Basic Concept of Nanotechnology*, Proc. Int. Conf. Prod. Eng. (1974).
- [4] S. Chaturvedi, P. N. Dave and N. K. Shah, *Journal of Saudi Chemical Society*, **16**(3), 307 (2012).
- [5] S. Mandegarzar, J. B. Raoof, S. B. Hosseini and R. Ojani, *Electrochimica Acta*, **190**, 729 (2016).
- [6] J. Durst, C. Simon, F. Hasche and H. A. Gasteiger, *J. Electrochem. Soc.*, **162**(1), F190 (2015).
- [7] G. Garcia, V. Baglio, A. Stassi, E. Pastor, V. Antonucci and A. S. Aricò, *J. Solid State Electrochem.*, **11**(9), 1229 (2007).
- [8] J. Liu, J. Cao, Q. Huang, X. Li, Z. Zou and H. Yang, *J. Power Sources*, **175**(1), 159 (2008).
- [9] R. Wang, B. Wei, H. Wang, S. Ji, J. Key, X. Zhang and Z. Lei, *Ionics*, **17**(7), 595 (2011).

- [10] C. Busó-Rogero, J. Solla-Gullón, F. J. Vidal-Iglesias, E. Herrero and J. M. Feliu, *J. Solid State Electrochem.*, **1** (2015).
- [11] S.-H. Li, Y. Zhao, J. Chu, W.-W. Li, H.-Q. Yu, G. Liu and Y.-C. Tian, *Front. Environ. Sci. Eng.*, **7**(3), 388 (2013).
- [12] P. Waszczuk, T. M. Barnard, C. Rice, R. I. Masel and A. Wieckowski, *Electrochem. Commun.*, **4**(7), 599 (2002).
- [13] Y. Chen, C. W. Li and M. W. Kanan, *J. Am. Chem. Soc.*, **134**(49), 19969 (2012).
- [14] J. Park, J. Joo, S. G. Kwon, Y. Jang and T. Hyeon, *Angew. Chem. Int. Ed.*, **46**(25), 4630 (2007).
- [15] D. König, K. Richter, A. Siegel, A.-V. Mudring and A. Ludwig, *Adv. Funct. Mater.*, **24**(14), 2049 (2014).
- [16] F. Masini, P. Hernandez-Fernandez, D. Deiana, C. E. Strebel, D. N. McCarthy, A. Bodin, P. Malacrida, I. Stephens and I. Chorkendorff, *Phys. chem. chem. phys.*, **16**(48), 26506 (2014).
- [17] M. Nie, K. Sun and D. D. Meng, *J. Appl. Phys.*, **106**(5), 054314 (2009).
- [18] P. Shah and A. Gavrin, *J. Magn. Magn. Mater.*, **301**(1), 118 (2006).
- [19] T. Torimoto, K.-I. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka and S. Kuwabata, *Appl. Phys. Lett.*, **89**(24), 243117 (2006).
- [20] Y. Hatakeyama, S. Takahashi and K. Nishikawa, *J. Phys. Chem. C*, **114**(25), 11098 (2014).
- [21] Y. Hatakeyama, K. Onishi and K. Nishikawa, *RSC Adv.*, **1**(9), 1815 (2011).
- [22] E. Vanecht, K. Binnemans, J. W. Seo, L. Stappers and J. Franssaer, *Phys. chem. chem. phys.*, **13**(30), 13565 (2011).
- [23] S. Suzuki, T. Suzuki, Y. Tomita, M. Hirano, K.-I. Okazaki, S. Kuwabata and T. Torimoto, *CrystEngComm*, **14**(15), 4922 (2012).
- [24] K.-I. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata and T. Torimoto, *Chem. Commun.* (6), 691 (2008).
- [25] Y. Oda, K. Hirano, K. Yoshii, S. Kuwabata, T. Torimoto and M. Miura, *Chem. Lett.*, **39**(10), 1069 (2010).
- [26] T. Suzuki, S. Suzuki, Y. Tomita, K.-I. Okazaki, T. Shibayama, S. Kuwabata, T. Torimoto, *Chem. Lett.*, **39**(10), 1072 (2010).
- [27] T. Suzuki, K.-I. Okazaki, S. Suzuki, T. Shibayama, S. Kuwabata and T. Torimoto, *Chem. Mater.*, **22**(18), 5209 (2010).
- [28] T. Suzuki, K.-I. Okazaki, T. Kiyama, S. Kuwabata and T. Torimoto, *Electrochemistry*, **77**(8), 636 (2009).
- [29] O. P. Khatri, K. Adachi, K. Murase, K. I. Okazaki, T. Torimoto, N. Tanaka, S. Kuwabata and H. Sugimura, *Langmuir*, **24**(15), 7785 (2008).
- [30] K.-I. Okazaki, T. Kiyama, T. Suzuki, S. Kuwabata, T. Torimoto, *Chem. Lett.*, **38**(4), 330 (2009).
- [31] S. Suzuki, Y. Ohta, T. Kurimoto, S. Kuwabata and T. Torimoto, *Phys. chem. chem. phys.*, **13**(30), 13585 (2011).
- [32] Y. Hatakeyama, T. Morita, S. Takahashi, K. Onishi and K. Nishikawa, *J. Phys. Chem. C*, **115**(8), 3279 (2011).
- [33] H. Wender, L. F. de Oliveira, A. F. Feil, E. Lissner, P. Migowski, M. R. Meneghetti, S. R. Teixeira and J. Dupont, *Chem. Commun.*, **46**(37), 7019 (2010).
- [34] H. Wender, R. V. Goncalves, A. F. Feil, P. Migowski, F. S. Poletto, A. R. Pohlmann, J. Dupont and S. R. Teixeira, *J. Phys. Chem. C*, **115**(33), 16362 (2011).
- [35] Y. Shishino, T. Yonezawa, S. Udagawa, K. Hase and H. Nishihara, *Angew. Chem. Int. Ed.*, **50**(3), 703 (2011).
- [36] J. Siegel, O. Kvítek, P. Ulbrich, Z. Kolská, P. Slepíčka and V. Švorčík, *Mater. Lett.*, **89**, 47 (2012).
- [37] Y. Ishida, R. Nakabayashi, M. Matsubara and T. Yonezawa, *New J. Chem.*, **39**(6), 4227 (2015).
- [38] Y. Shishino, T. Yonezawa, K. Kawai and H. Nishihara, *Chem. Commun.*, **46**(38), 7211 (2010).
- [39] I. Y. Cha, M. Ahn, S. J. Yoo and Y.-E. Sung, *RSC Adv.*, **4**(73), 38575 (2014).
- [40] T. Tsuda, K. Yoshii, T. Torimoto and S. Kuwabata, *J. Power Sources*, **195**(18), 5980 (2010).
- [41] K.-I. Okazaki, J. Sakuma, J.-I. Yasui, S. Kuwabata, K. Hirahara, N. Tanaka and T. Torimoto, *Chem. Lett.*, **40**(1), 84 (2011).