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Synthesis of Pt nanoparticles as catalysts of oxygen reduction with microbubble-assisted low-voltage and low-frequency solution plasma processing

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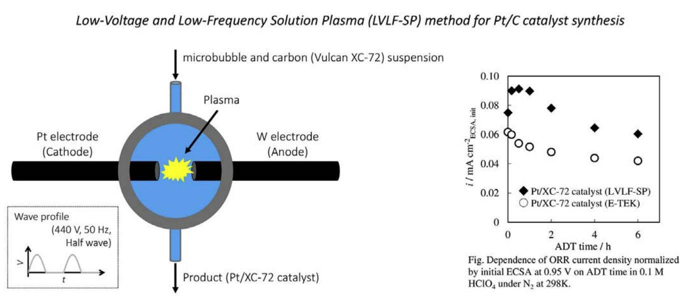
HIGHLIGHTS

- A new method called LVLF-SP was developed for Pt nanoparticles (PtNPs).
- LVLF-SP is one of the solution plasma processings.
- Microbubble suspension is a key technique to stabilize the plasma emission.
- LVLF-SP can produce about 3 nm carbon supported PtNPs directly and successively.
- Pt/XC72 obtained by LVLF-SP had higher oxygen reduction activity than commercial one.

GRAPHICAL ABSTRACT



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ABSTRACT

In the preparation of metallic nanoparticles by conventional solution plasma (SP) techniques, unstable plasma emission becomes an issue when the voltage and frequency of the waves applied between two electrodes placed in solution are lowered to avoid the boiling of the solution. In this study, we confirm that, in the presence of microbubbles, plasma is generated stably at low voltage (440 V) and low frequency (50–100 Hz) and small-size (≤10 nm) Pt nanoparticles (PtNPs) are synthesized in succession using a flow cell. The smallest PtNPs, ~3.3 nm in diameter, are obtained using half-wave rectification, a tungsten wire anode, and a platinum wire cathode. The PtNPs are characterized by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and thermogravimeter-differential thermal analysis. The oxygen reduction reaction (ORR) is investigated in 0.1 M $HClO_4$ solution on carbon-supported PtNPs using a rotating ring-disk electrode. The catalytic activities per initial electrochemical active surface area of the carbon-supported PtNPs synthesized employing the low-voltage, low-frequency (LVLF)–SP technique is higher than that of the commercially available 20 wt% Pt on Vulcan XC-72R. These results indicate that the LVLF-SP technique is a promising approach to producing carbon-supported PtNPs that catalyze ORR with low energy consumption.

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1. Introduction

Solution plasma (SP) is generated in the liquid phase when high voltage and high-frequency waves are applied between two electrodes placed in solution. In the situation, the solution near the electrodes is heated to generate a gas phase, where plasma is formed [1,2]. SP-based techniques enable to simplify the synthesis of nanomaterials, which is achieved in the absence of reagents like reductants or oxidants. Recently, many nanomaterials (e.g. metal nanoparticles [2–18], metal oxide nanoparticles [19–22], and elemental-carbon-based materials [23–25]) have been synthesized employing SP-based techniques. In addition, SP-based techniques have been successfully applied to the synthesis of metal oxide composites [26,27], the treatment and depolymerization of polymers [28–32], the treatment of water [33], and the production of fuel gas [34].

A typical application of Pt nanoparticles (PtNPs) is the catalyst of an oxygen reduction reaction (ORR) that takes place at the cathode of polymer electrolyte fuel cells (PEFCs). Although there are some reports of the synthesis of PtNPs using the SP technique [13,25], an expensive power source is needed in the cases to obtain the high voltage and high frequency necessary for SP generation. In addition, it is difficult to keep reaction conditions constant during the preparation of PtNPs using the conventional SP techniques, because the energy applied to the solution of a reaction cell is so large that the solution starts boiling within about 1 min. Hence, our group developed an SP-based technique that makes use of low voltage (440 V) and low frequency (50–100 Hz) to prevent the solution from boiling and reduce the cost of the procedure [35]. In a previous study, we successfully synthesized the Pt/XC72 catalysts using an SP-based technique. However, the frequency of the plasma emission was unstable, and the size of the Pt particles produced (~20 nm) was not sufficiently small for the PEFC electrode catalyst, so that the mass catalytic activity for ORR of the particles produced was much lower than that of the commercially available 20 wt% Pt/XC-72R (E-TEK).

In this manuscript, we describe a new SP-based synthetic procedure that employs a low-voltage and low-frequency electric source together with microbubbles to aid the synthesis of PtNPs successively by using a flow cell for application to electrode catalysts. In such conditions, the solution does not boil, and the microbubbles formed assist stable plasma emission. We optimized the experimental conditions — including the layout of the electrodes — to control SP generation. In the present study, a carbon-supported PtNP catalyst was also synthesized using the optimized low-voltage, low-frequency (LVLF)-SP technique

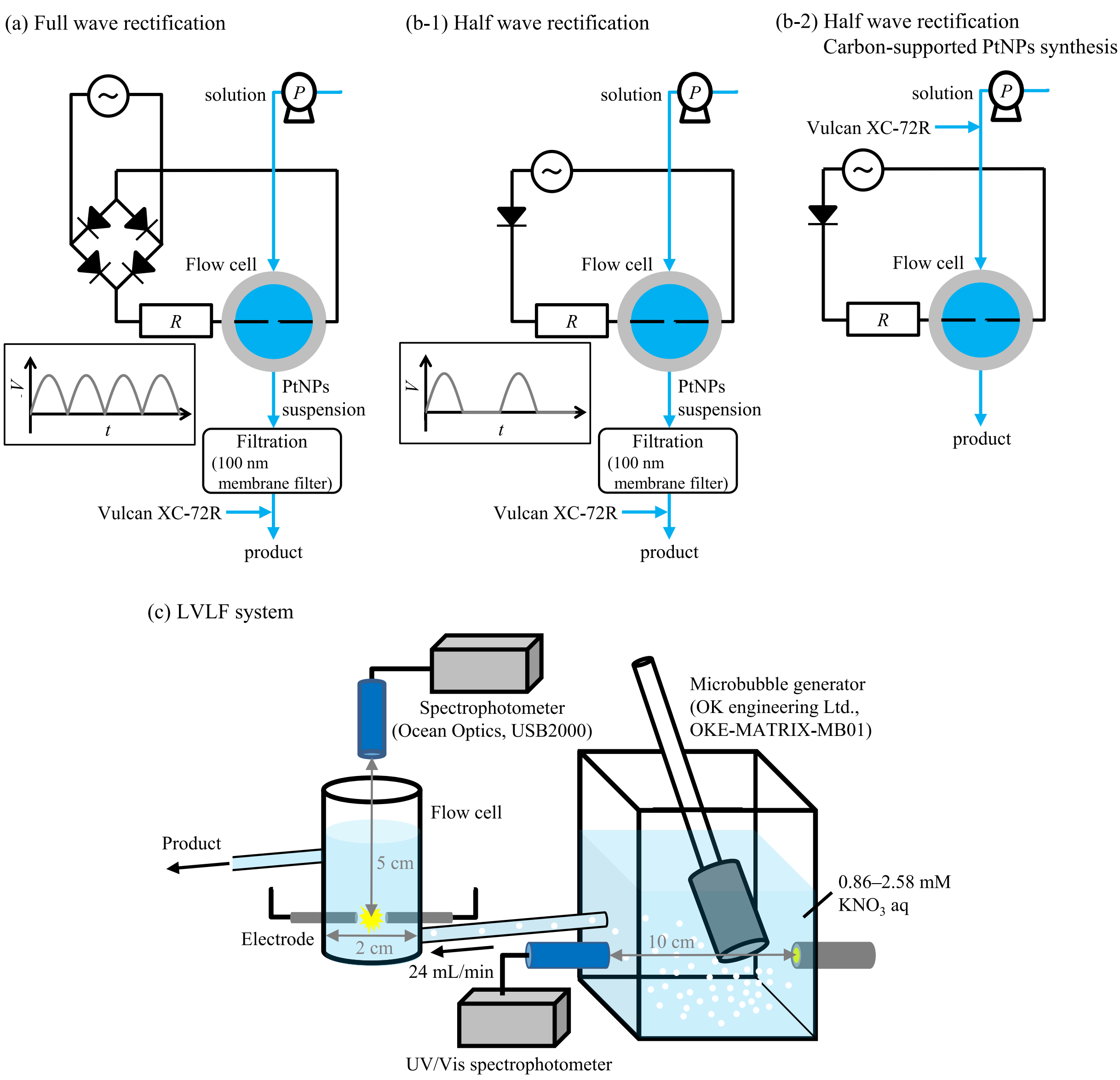

Fig. 1. Electric circuits for (a) full wave rectification and (b) half wave rectification. (c) Schematic view of a LVLF-SP system for the synthesis of PtNPs.