Advanced Laser Science Research Section

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1. Introduction

Laser is a very powerful tool to synthesize/modify the target materials and also remotely probe the various dynamics. This year we have studied the properties of metal-polymer nanocomposites with a focus on its molecular weight, and developed a simple but efficient technique to detect and also size nanoparticles in bulk water.

2. Probing the concentration profile of dissolved gas in proximity to the electrode during hydrogen gas evolution

Hydrogen evolution reaction (HER) through water electrolysis is considered to be one of the promising methods to store renewable energy. While water electrolysis is a well-known process, it does not mean that realization of high efficiency for the practical use is a trivial task. From the material science viewpoint, developing efficient and durable electrocatalysts is obviously an important issue. From the physical chemistry and chemical physics viewpoint, HER involves important bubble dynamics such as nucleation, detachment, and transport of bubbles. The concentration of the dissolved gas in close proximity to the electrode increases and reaches supersaturation during electrolysis, and depending on the supersaturation level a tiny local fluctuation triggers the nucleation of gas bubbles. Needless to say, the concentration of dissolved hydrogen gas in proximity to the electrode shows a gradient, and up to what distance and size the bubbles can grow with what rates depends on the electrolysis conditions. Clearly, such information is crucial toward the efficient HER. Traditionally, electrochemical methods with micro/nanoelectrodes are used to study nucleation on the electrode. However, such methods cannot be applied under the presence of bubbles, since it hinders the accurate monitoring of nucleation dynamics.

Knowing the above we have developed a new technique to probe the concentration profile of the dissolved gas during HER, which itself is useful not only to understand the bubble nucleation dynamics but also to optimize the electrolysis conditions. The setup of our detection system is shown in Fig. 1. We employ an Ni wire and Pt mesh as a working and counter electrodes, respectively. Both electrodes are fixed on a squared PTFE frame, and immersed in the 60 mL KOH solution at 0.1 M in an acrylic cuvette (Fig. 1(a)). The working electrode is at the lower position than the counter electrode (Fig. 1(b)) to secure a clear view of hydrogen bubbles without the presence of oxygen bubbles. To observe bubbles we take the shadowgraphic images of bubbles in proximity to the Ni wire electrode with a fast camera under the LED illumination through a telecentric lens.

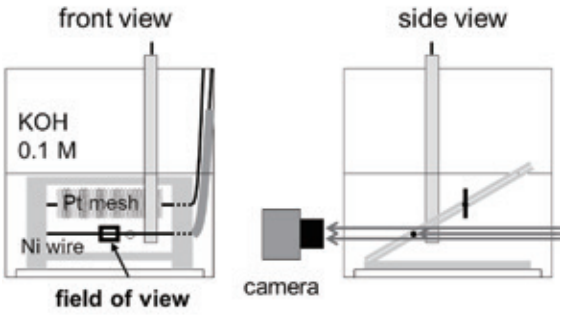

Fig. 1 Experimental setup to optically detect the electrolysis bubble. (a) front view and (b) side view. As shown in (b) bubbles are illuminated from behind the wire electrode by LED.

Fig. 2(a) shows an example of hydrogen bubbles in proximity to the Ni wire electrode under the constant current mode of −8 mA (equivalent to the current density of -85 mA/cm^2). There are a few big bubbles which hinder the image analysis, and hence we focus on the area, defined by the two dashed vertical lines of Fig. 2(a), to analyze the bubble dynamics. To evaluate the radii and growth rates of individual bubbles we have developed a home-made software. Once these quantities have been obtained from the image analysis of bubbles, we can use the diffusion model to extract the concentration of dissolved gas as a function of distance from the electrode, and the corresponding results are shown in Fig. 2(b). When the bubbles are too close to the wire electrode it is not easy to isolate tiny bubbles from the electrode through the image analysis described above. Under the current experimental conditions, the closest distance for the image analysis of bubbles is about 15 μm from the electrode. Therefore, we perform the linear fittings to the concentration (left axis of Fig. 2(b)) and extrapolate the fitted line to distance zero to obtain the concentrations of dissolved hydrogen gas on the electrode to be 30.9±1.8 mM for the current density of −85 mA/cm^2. We point out that

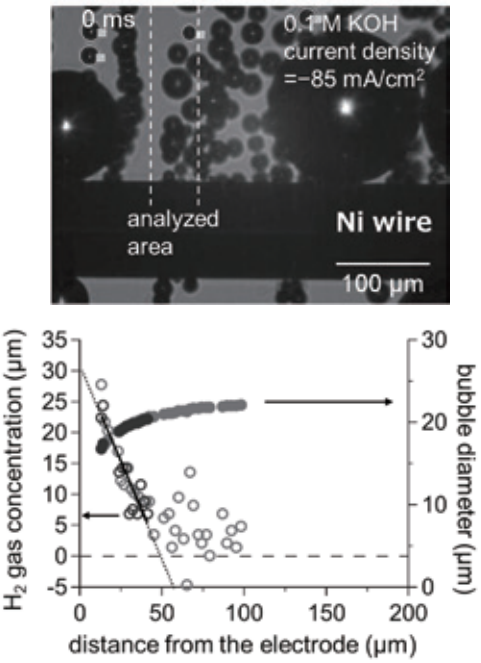

Fig. 2 Analysis of H_2 gas concentration in proximity to the Ni wire electrode. (a) Optical image and (b) H_2 gas concentration obtained from the bubble growth rate at the different distances from the electrode.

this concentration is much lower than the one expected for the classical bubble nucleation with a nanoelectrode, and hence it suggests that the bubble nucleation mechanism with a macroscopic electrode like our case is not classical. A further study is necessary to clarify this point.

3. First observation of the formation of nanoparticles inside the ablation by laser scattering

Use of laser ablation in liquid is one of the flexible techniques to produce various kinds of nanoparticles. However, the physical mechanism of nanoparticle formation upon laser ablation in liquid is not yet well understood. One powerful technique to tackle this problem is small-angle x-ray scattering. Application of the laser-scattering technique in a similar context faces some difficulties, since the curved bubble surface does not allow a probe laser to go into the bubble, and even if it goes into the bubble the extremely weak

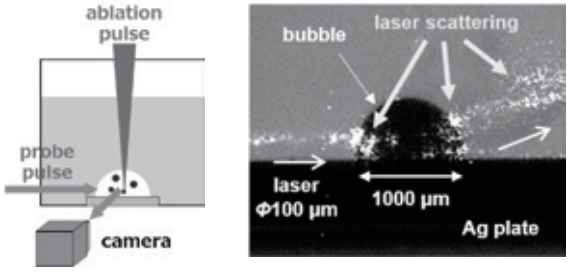

Fig. 3 Experimental setup for the time-resolved optical detection of single nanoparticles by laser scattering.

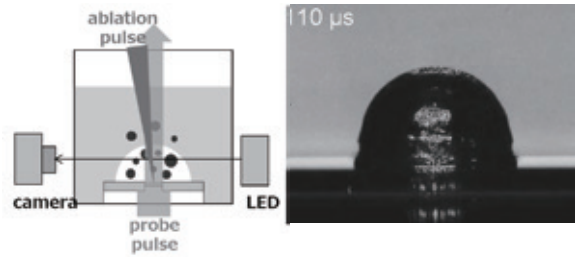

Fig. 4 Our setup to optically observe the inside of ablation bubble by laser scattering. A probe pulse is introduced into the bubble through a flat transparent window produced by laser ablation of thin metallic film on a glass substrate.

scattering signal from inside the bubble is overwhelmed by the very strong reflection at the bubble surface (Fig. 3). We have solved those problems by sending the probe laser into the bubble through a laser-induced flat transparent window, and demonstrate the clean observation of laser-scattering signals from the inside of the ablation bubble (Fig. 4). We have found the signature of nanoparticle formation around the two areas inside the bubble, that is, around the central area and apex inside the bubble (Fig. 4(b)). By changing the delay time between the ablation and probe pulses until the bubble collapses (<150 μs after the ablation pulse) we have found that the scattering signals originating from the central area of the bubble persistently stay throughout the entire growth and shrinkage stages of the bubble. More interestingly, the scattering signals originating from the apex inside the bubble gradually emerges after the bubble size becomes maximum, and they become brighter during the shrinkage stage. Those findings are consistent with the scenario of nanoparticle formation obtained by small-angle x-ray scattering experiments.

To better understand where in the bubble the scattering light comes from, we consider the inverse light scattering problem (Fig. 5), and find that the scattering signal from point P1 comes from the scatterers located at point Q in the right panel of Fig. 5. The scattering signal from point P2 can be understood as scattering light that has reached the camera directly from point Q without refraction. This is the first clear observation of nanoparticle formation insider the ablation bubble by laser scattering, which allows us to track the nanoparticle formation process.

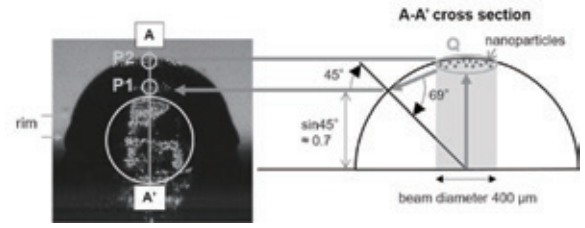

Fig. 5 (Left) Laser scattering image superimposed on the shadowgraph image. (Right) Optical path of the scattering light cut at A-A' cross section.

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Publications

K. Ando, Y. Uchimoto, T. Nakajima, Single-shot laser scattering technique refined for the real-time monitoring and sizing of individual nanoparticles and nanobubbles in bulk water, Optics Letters, 45, 12, 3321-3324, 2020

K. Ando, T. Nakajima, Clear observation of the formation of nanoparticles inside the ablation bubble through a laser-induced flat transparent window by laser scattering, Nanoscale, 12, 17, 9640-9646, 2020

K. Ando, Y. Uchimoto, T. Nakajima, Concentration profile of dissolved gas during hydrogen gas evolution: an optical approach, Chemical Communications, 56, 92, 14483-14486, 2020

K. Kashihara, Y. Uto, T. Nakajima, Size-controlled in situ synthesis of metal–polymer nanocomposite films using a CO2 laser, Polymer Bulletin, 2020

K. Hata, Q.S. Liu, T. Nakajima, Natural convection heat transfer from vertical 9 x 9 rod bundles in liquid sodium, Heat and Mass Transfer, 2020