# Feature Article

## Development of a Large Capacity Liquid Vaporization System Using the Bubbling Method

### — Achieving high accuracy through control of bubble diameter and liquid temperature distribution —

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As solar cells undergo rapid market expansion and production increases, a more stable supply of large volume materials is demanded. Solar cell manufacturing processes make heavy use of substances in liquid state at room temperature, which are then vaporized and injected into the manufacturing process. The vaporization system in this study makes use of bubbling and is able to heat and vaporize 100 L of liquid material by controlling the air bubble diameter to 1 mm during bubbling and by optimizing the heating configuration for the liquid. This paper introduces liquid vaporization technology and presents an explanation of the vaporization system together with experimental results.

## Introduction

Photovoltaic generation has recently been attracting attention throughout the world, and systems that can convert sunlight to electricity using solar cell panels are spreading globally. The solar cells that make up these solar panels can be divided into silicon-based systems and chemical compound systems. Silicon systems can be further divided into crystalline and thin-film solar cells, and chemical compound solar cells can be classified into organic or inorganic cells. Thin-film solar cells that are manufactured by applying the technology in this study are composed of a glass substrate, transparent electrode film, a thin-film electric generation layer, and rear surface electrodes. A transparent electrode is a type of electrode made from substances that have light (visual) transparency and electrical conduction properties. Oxide films such as $SnO_2$, ZnO, and $TiO_2$ are predominantly used today for transparent electrode films. These oxide films are formed by the CVD (chemical vapor deposition) method and use vaporization materials that are in a liquid state at room temperature.

Vaporization of liquids is typically performed by the following steps: let gas flow into the liquid material then vaporize the liquid by making it bubble—the “bubbling method.” The advantages of this bubbling method are the simple layout of the process and the low expense to build the system. One shortcoming, however, is in accuracy, specifically the large divergence between the actual amount vaporized and the theoretical amount. This divergence arises from the accuracy of the carrier gas flow rate and actual temperature of the liquid material combined with pressure gauge and thermometer accuracy. Furthermore, liquid temperature control becomes more difficult as the amount vaporized increases, which causes the actual amount vaporized and the theoretical amount to diverge even more. Highly accurate vaporization amounts are being demanded in recent years in order to reduce the cost and improve the performance of solar cells.

In consideration of cost, we used our own high-accuracy mass flow controller (MFC) to regulate the carrier gas flow rate, a critical factor for performance. In the area of liquid temperature control, HORIBA STEC has developed a bubbling tank and a heating control method that together allow the ideal temperature regulation of liquids and has employed this vaporization system to deliver a stable supply of vaporized gas in a practical application.

## Design of a Vaporization Device Using the Bubbling Method

The principle of vaporization using the bubbling method is to let the gas flow into the liquid and then vaporize the liquid. This method has been widely used and commercialized. The material concentration and amount vaporized in the gas that passes through the liquid under the bubbling method follow the relationships in Formula 1 and 2.

Material concentration = Saturated vapor pressure of the liquid / Total pressure ······································ (1)

Vaporization amount = Total flow rate after liquid pass-through × Material concentration ························ (2)

From the relationship in Formula 1 and 2, the factors having the greatest influence on the vaporization amount after bubbling are: 1) variation in liquid temperature by vaporization heat, 2) measurement errors for the carrier gas flow rate, and 3) pressure variation. Normally, the factor with the greatest influence on vaporization accuracy is the instability of the amount vaporized as a result of liquid temperature variation. For this study, we developed a bubbling system that sets the liquid temperature variation for a large capacity bubbling method to be within ±1 °C.

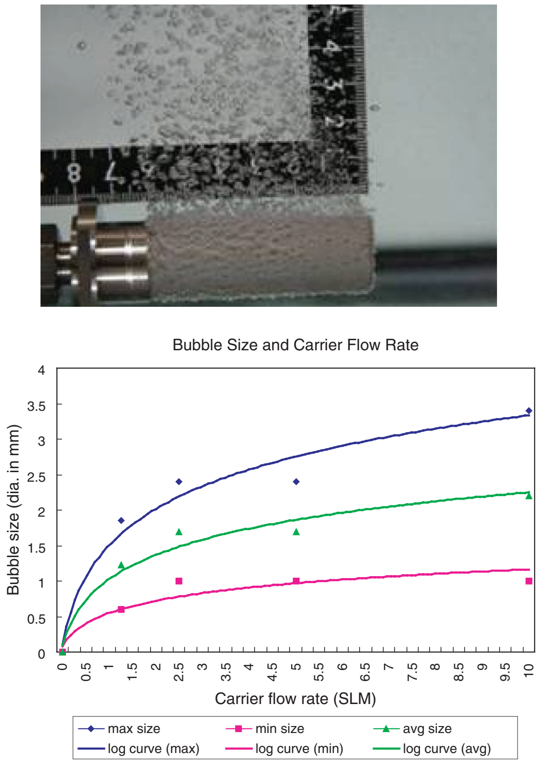

Figure 1 Bubble generator position and flow rate

***Bubble generator.*** To keep the temperature distribution within ±1 °C, we considered the air bubble diameter of carrier gas for bubbling that would improve the vaporization stability. Figure 1, the conditions immediately after the bubble generation area, shows the variation in air bubble diameter as a result of carrier gas flow rate and bubble position. After generation, bubble fusion causes bubble diameter to grow as the bubbles pass through the liquid. A bubble generator location that fits the vaporization amount was selected based on correlation data between carrier gas flow rate and bubble diameter, as shown in Figure 1. The bubble generator was designed with an attachment structure that allows it to be placed an arbitrary distance from the inner wall of the bubble tank.

***Pre-heater.*** When the carrier gas reaches a bubble state and passes through the liquid, the liquid temperature falls due to the carrier gas flow rate. For this reason, the carrier gas must be preheated before entering the bubbling tank and then passed into the bubbling tank. The needed function of a pre-heater to heat the carrier gas should have: 1) a gas temperature after pre-heating that is independent of flow rate, 2) the ability to pass high-purity clean gas, and 3) a compact design. HORIBA STEC's gas pre-heater fulfills these requirements, as shown by the measurements of carrier gas flow rate and pre-heated gas temperature depicted in Figure 2.

***Vaporizer and heater.*** The vaporization system has a single structure cast from stainless steel tubes and an aluminum heater and can secure a flow path for passing

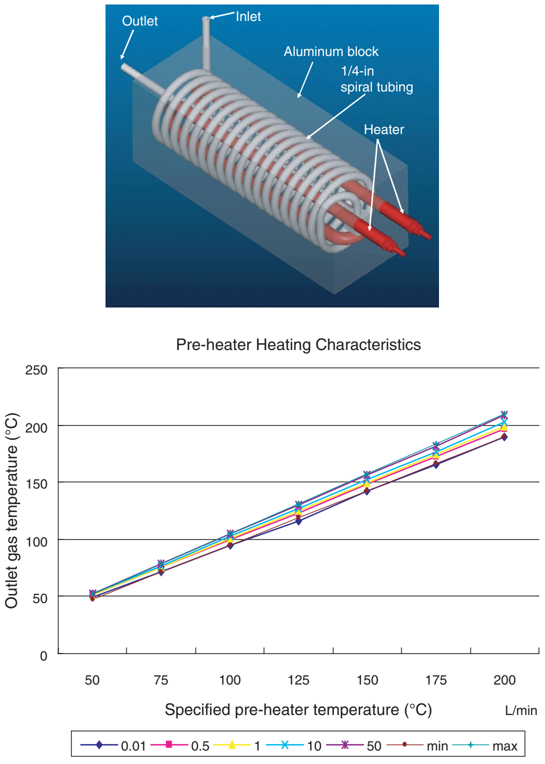

Figure 2 Pre-heater layout and heating characteristics

high purity gas. The total capacity of the bubbling tank was set to 100 L with the objective of handling a series of vaporizations over an extended period with a large flow of carrier gas. One implication of using a large capacity tank is that peripheral heating is be unable to offer sufficient heat to the center region to regulate the internal liquid temperature. Also, the liquid temperature would fall because the vaporization deprives the liquid of latent heat. Therefore, we added a heater for heating the central region of the container using an indirect configuration, as shown in Figure 3. The indirect structure allows the heater to be replaced for a heater wire break or similar event without exposing the bubbling tank to the atmosphere, and furthers the goal of keeping down system costs by incorporating a general purpose heater instead in the design instead of a special-made heater. The selected heater has the ability to control the temperature at 100 °C±5 °C and 200 °C±10 °C for an $N_2$ carrier gas flow rate in the 10 ml/min to 50 l/min range.

***Temperature control.*** The bubbling tank's trunk heater performs feedback control through a temperature sensor that measures the liquid temperature. In order to create a low-water cut-off and prevent elevated heater temperatures when raising the temperature from room temperature, we employed a temperature control scheme, called "cascade temperature control," in which the heater itself was under temperature control at the same time. Another temperature control problem is that a tall bubbling tank design will create a vertical temperature distribution with an upper layer having a high liquid temperature and a lower layer having a comparatively low liquid temperature. An agitator is normally used to create a uniform liquid temperature distribution in the bubbling tank, but the forced circulation has the disadvantage of bubble fusion. We took advantage of the air bubble movement during bubbling to solve this problem.

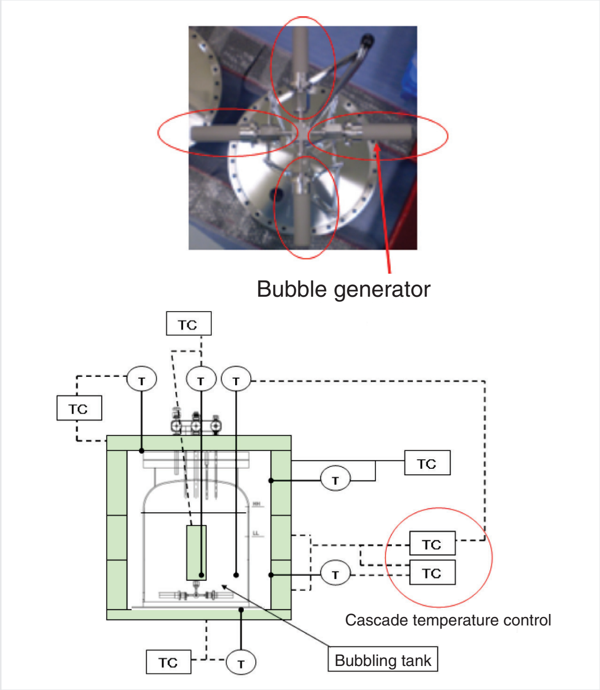

Figure 3 Bubbling tank layout

## Bubbling Method Vaporization Experiment

***Methods and Materials.*** The vaporization performance of the system with the layout as shown in Figure 4 was evaluated under the following conditions:

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|---|---|
| Liquid material | Isopropyl alcohol (IPA) |
| Carrier gas | $N_2$ |
| Controlled liquid temperature | 75 °C |
| Pre-heater temperature | 75 °C |
| Carrier gas flow rate | 10 l/min |
| Secondary pressure after vaporization | Atmospheric pressure |

The liquid temperature in the bubbling tank was monitored at approximately 40 points, and the temperature at each monitoring point was evaluated for whether it stabilized within 75 °C±1 °C. Vaporization performance was assessed by checking the carrier gas concentration after vaporization. Flow rate measurements taken with a mass flow meter (MFM) were evaluated, and

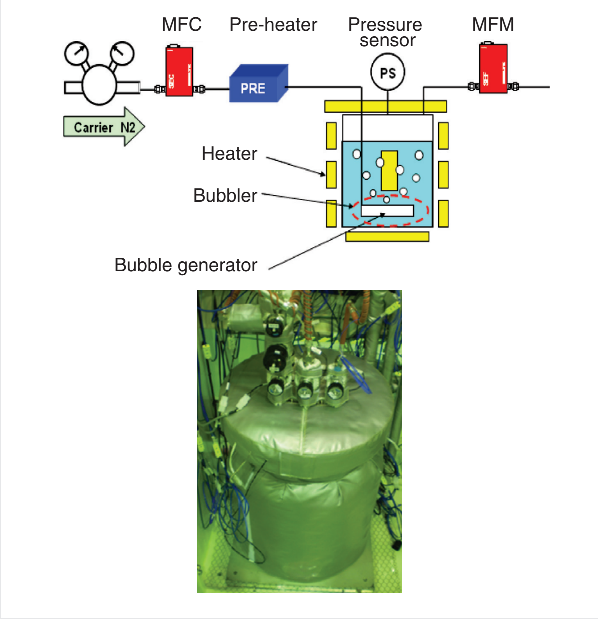

Figure 4 Bubbling method (flow diagram, bubbler external view)

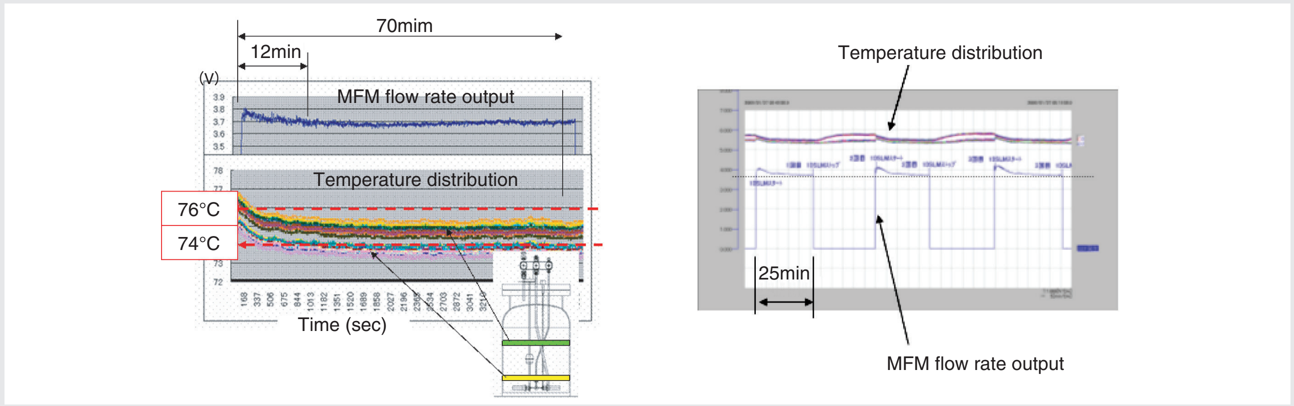

Figure 5 Liquid temperature distribution – evaluation results

if the MFM reported a constant flow rate reported, then the concentration of the vaporized gas was judged to be constant. We then repeated the experiment 3 times and assessed the vaporization. It should be noted, however, that although this assessment testing used IPA for verification, actual solar cell manufacturing processes use different liquids.

***Results.*** Experimental results are shown in Figure 5. First, the liquid temperature rose immediately after bubbling began. Because the carrier gas was not allowed to flow, the temperature stabilized at approximately 5 °C higher than the specified temperature and the liquid temperature rose as a result of agitation by bubbling. After 4 minutes, the liquid temperature at each measurement point stabilized by converging to within ±1 °C of the 75 °C control temperature. The flow rate monitored by the MFM exhibited similar behavior to the liquid temperature: a high flow rate immediately after vaporization that then stabilized under steady temperature conditions. From these results, we learned that the concentration status can be determined by monitoring the flow rate reported by an MFM. We believe the actual flow rate can be measured by preparing a flow rate calibration curve for MFM output based on known gas concentrations.

As a result of this experiment, we could confirm the temperature stability and that the measured flow rate by the MFM could be reproduced. If we stopped the carrier gas, the liquid temperature would rise. Specifically, because the vaporization causes the agitation of the liquid to stop, a temperature differential arises between the upper and lower layers as under normal conditions, and the warm liquid moves to the upper layer. Another finding is that the actual vaporization amount temporarily increases over the specified vaporization amount at the initial occurrence of vaporization.

The system design must optimize the PID values of the temperature controller and select the most appropriate heating capacity for the heater.

## Conclusion

In this study, we developed a system for stable supply of vaporized gas. This system uses the bubbling method to take advantage of agitation effects from bubbling the liquid in a bubbling tank, adopts an optimal heating configuration, and enforces a uniform temperature distribution throughout the liquid. We proceeded with development on critical equipment, from a performance perspective, for improving the accuracy of the vaporization amount. This development takes the form of a system comprising a HORIBA STEC mass flow controller and a gas heating unit.

The current study was aimed at solar cell manufacturing, but we believe that future applications will be able to apply a gas supply system that vaporizes liquid through the bubbling method to other fields. In the area of gas supply methods using liquid vaporization, Horiba possesses vaporization technology that uses methods other than the bubbling method, such as vaporization without carrier gas. In the area of liquid materials, we are developing technology that can safely and accurately vaporize such liquid material as poisons, flammable liquids, and pyrophoric materials that have seen frequent use in recent years.

Through research and development of liquid vaporization technology, HORIBA STEC willingly takes up the challenge to make a contribution to the environment through solar cells and other technologies.

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