



# Direct measurements of local current distributions on electrodes covered with thin liquid electrolyte films



Atsunori Ikezawa, Kohei Miyazaki\*, Tomokazu Fukutsuka, Takeshi Abe

Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

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## ABSTRACT

Thin liquid electrolyte films are frequently used in electrochemical systems, such as energy devices and sensors, where they play an important role in determining the performance of such devices. However, it is difficult to experimentally determine the electrochemical behavior of these thin liquid films on electrodes. Here we investigated the uneven distribution of currents on an electrode covered with a thin liquid electrolyte film using a segmented Pt array electrode. A combination of experimental and simulation studies revealed that local ionic resistances governed the active positions of electrodes for the oxygen reduction reaction. These results demonstrate that segmented array electrodes are powerful tools for investigating the unique electrochemical features of thin liquid electrolyte films.

## 1. Introduction

Thin liquid electrolyte films are unique reaction fields, since the transport of multiple components (e.g., gas, ions, solvents, and electrons) is restricted along and across the films. Since the path along the film is restricted, the transport of ions and solvents in thin films is slower than that in bulk electrolyte solutions. In contrast, the transport of gases across thin films is accelerated because of the shorter paths. These features characterize many important reaction fields, especially for electrochemical systems. For example, corrosion systems [1–4], electrochemical sensors [5], lab-on-a-chip devices [6], and gas diffusion electrodes [7–11] have all been actively studied.

Thin liquid films can be grouped into two types: isolated liquid films and liquid films in contact with a bulk solution. Isolated films have often been investigated in studies on atmospheric corrosion [1–3]. Metal corrosion and oxygen reduction occur in the same isolated liquid film. On the other hand, films in contact with a bulk solution have been studied as a model reaction field for gas diffusion electrodes [7–11] and as a reaction field for liquid line corrosion [4]. The main difference between these two liquid films may be the uniformity of the reaction: while electrochemical reactions occur uniformly in isolated films, the reaction rates diverge in liquid films in contact with bulk solutions. Ions and gas molecules move across the border between films and bulk solutions, and a position-dependent scheme for reaction rates should be considered to understand the electrochemical behavior.

Previously, we have studied thin liquid electrolyte films that formed on partially immersed Pt electrodes [10]. By changing the vertical

position of an electrode, the vertical length of a thin liquid film could be controlled, and electrochemical measurements were performed simultaneously. We found that the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) occurred in limited and different areas, although they were reverse reactions. However, since it was impossible to monitor local currents, the details of the current distribution in thin liquid films have not yet been unveiled. Therefore, direct measurements of local currents in thin liquid films would be of great importance for improving the performance of various electrochemical devices.

In this study, we investigated the electrochemical behavior of thin liquid electrolyte films using a segmented Pt array electrode. By monitoring the current for each channel, the current distributions in thin liquid films could be directly measured. We combined these findings with the results of a simulation study, and discuss the factor that most strongly influences electrochemical oxygen reactions (ORR and OER) in thin liquid films.

## 2. Experimental

Segmented Pt array electrodes were fabricated by electron-beam lithography. As shown in Fig. 1(a), 10 channels of platinum ( $0.9 \times 10$  mm, 100 nm thickness) were arranged with a 0.1 mm gap on a silica glass substrate. Each channel was connected to a conducting platinum layer, the surface of which was masked with an epoxy resin, and were referred to as channels (CH) 1–10 from the bottom to the top of the array electrodes. The vertical position of the array electrode in an

\* Corresponding author.

E-mail address: [myzkohei@elech.kuic.kyoto-u.ac.jp](mailto:myzkohei@elech.kuic.kyoto-u.ac.jp) (K. Miyazaki).

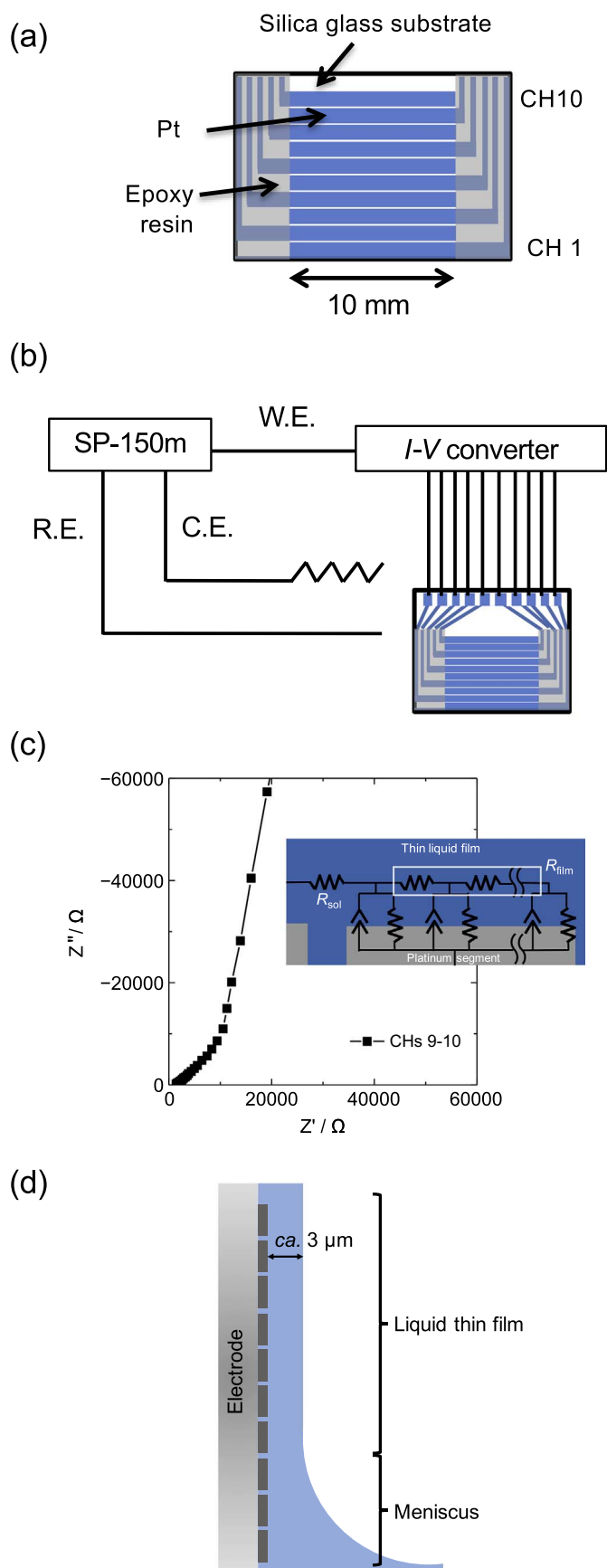


Fig. 1. Schematic illustrations of (a) the Pt segmented electrode, (b) the electrochemical setup, (c) Nyquist plot and the equivalent circuit model, and (d) the thin liquid film.

electrochemical cell was manipulated with a micrometer. For potentiostatic measurements, a homemade multi-channel  $I-V$  converter that applies the same potential to all channels and monitors the currents in all channels simultaneously, as shown in Fig. 1(b), was introduced. A Hg/HgO electrode (0.926 V vs. reverse hydrogen electrode, RHE) was used as a reference electrode, and Pt wire was used as a counter electrode. They were immersed in the bulk electrolyte solution. In addition, we performed AC impedance spectroscopy with an AC amplitude of 10 mV using two channels at an open circuit potential. Aqueous solutions of  $1.0 \text{ mol dm}^{-3}$  (M) KOH saturated with a gas mixture of  $O_2$  and Ar were used as an electrolyte solution. Electrochemical measurements were carried out using a voltammetry system (Bio-Logic, SP-150).

### 3. Results and discussion

The thickness of a liquid film is an important parameter that characterizes its properties. We carried out AC impedance measurements for two adjacent channels under an Ar atmosphere. At the bottom of liquid films, only blocking electrode behaviors appeared among CHs 1–3, which indicates that a thick liquid layer was formed at the bottom of the electrode and behaved like a bulk solution [2]. Above CH 4, every pair of adjacent CHs showed a straight line with an angle of  $45^\circ$ , which implies transmission line (TML)-type frequency dependence [12]. Typical Nyquist plots using CHs 9–10 are shown in Fig. 1(c). TML-type frequency dependence was widespread when thin liquid films with a uniform thickness were formed on electrodes [13]. We carried out curve-fitting using the equivalent circuit shown in Fig. 1(c) and a modeling program (Z-view, Scribner Associates Inc.) to determine the resistance of thin liquid films. The ionic resistance of thin liquid films ( $R_{film}$ ) was calculated as in our previous report [11]. The thickness of thin liquid films ( $\delta_{film}$ ) was calculated as [2]

$$\delta_{film} = \frac{H}{R_{film}\kappa W} \quad (1)$$

where  $\kappa$  is the ionic conductivity of KOH solutions [14],  $W$  is the width of the electrodes (10 mm), and  $H$  is the total height of two channels (1.8 mm). The thickness of the liquid films was calculated to be ca.  $3 \mu m$ , and was independent of the concentration of KOH. Generally, the thickness of a liquid electrolyte is governed by inertial and viscous forces [15]. Therefore, the liquid film formed on the segmented array electrode had a uniform thickness (between CHs 4 and 10) and a curved meniscus, as depicted in Fig. 1(d).

Next, we investigated oxygen reactions (ORR and OER) in thin liquid films. Fig. 2 shows the percentages of steady state currents at each channel. Overall currents were  $-0.400$  and  $0.400$  mA for ORR and

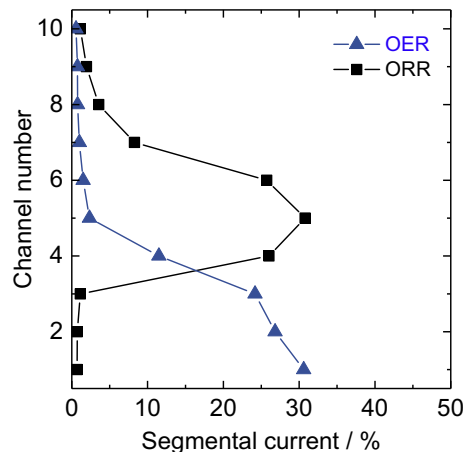


Fig. 2. Percentages of steady state segmental currents for ORR and OER under galvanostatic measurement (total current:  $-0.400$  and  $0.400$  mA, respectively) in  $1.0 \text{ M}$  KOH solution. Oxygen partial pressure was  $0.2 \text{ atm}$ .

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