

# In-Situ Electrochemical Quartz Crystal Microbalance Studies of Water Electrolysis at a Palladium Cathode

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## ABSTRACT

The in-situ electrochemical quartz crystal microbalance (EQCM) technique has been applied to study electrolysis of water containing 0.2 M LiClO<sub>4</sub> at Pd cathode. Decrease in resonant frequency was observed during the electrolysis. The decrease was attributed to the mass change involving hydrogen absorption into the palladium and lithium underpotential deposition, the mechanical stress change in the electrode, and the change in roughness of the electrode surface. The stress change, which may be caused by hydrogen uptake, was estimated using palladium film-coated AT- and BT-cut quartz crystal oscillators. The surface roughness change was observed by scanning electron microscopy and a number of cracks and holes were found. Underpotential deposition of lithium was observed in propylene carbonate containing 0.1 M LiClO<sub>4</sub> and 16 mg L<sup>-1</sup> water. Contributions of respective factors to the total frequency change was estimated.

## 1. Introduction

In the studies on electrolysis of LiOD/D<sub>2</sub>O or LiOH/H<sub>2</sub>O using a Pd cathode, it is important to elucidate the electrochemical reaction of proton and process of hydrogen absorption accompanied by change in mechanical stress and surface morphology of the Pd electrode. Electrochemistry of lithium on the Pd electrode should also be studied because it may play an important role for excess heat generation. These were examined by means of electrochemical quartz crystal microbalance technique.

## 2. Experimental

5.0 MHz AT- and BT-cut quartz crystal plates were coated with the same thickness (ca. 140 nm) of Pd thin-film by sputtering. Geometrical area of the piezoelectrically active electrode and electrochemically active one are 0.283 and 0.503 cm<sup>2</sup>, respectively. Electrochemical measurements were performed with a conventional three-electrode system in a 0.2 M LiClO<sub>4</sub> solution, pH of which has been adjusted to be 3.0 with HClO<sub>4</sub>. An Ag wire was employed as reference

electrode. Piezoelectric measurements were carried out as described elsewhere (Oyama *et al.*, 1990).

### 3. Results and Discussion

Correlation between frequency change ( $\Delta f$ ) of a quartz crystal oscillator and mass change on the electrode of the oscillator ( $\Delta m$ ) is reportedly as follows:

$$\Delta f = C \Delta m \quad (1)$$

where  $C$  is a constant. This equation is valid as long as the electrode is sufficiently rigid and the surface roughness and the mechanical stress of the electrode do not change. When the stress changes in the electrode of a quartz crystal oscillator, specific frequency of an AT-cut oscillator decreases with increasing stress, while that of a BT-cut oscillator increases. Frequency change caused by the lateral stress change ( $\Delta s$ ) has been formulated as follows, on the assumption that the vertical stress is negligible (EarNisse, 1973):

$$\Delta f_{AT} = (K_{AT} \Delta s / \tau_{AT} - \Delta m / \rho \tau_{AT}) f_{0AT} \quad (2)$$

$$\Delta f_{BT} = (K_{BT} \Delta s / \tau_{BT} - \Delta m / \rho \tau_{BT}) f_{0BT} \quad (3)$$

where  $K$  is a stress constant,  $\tau$  is the thickness of the quartz crystal, and  $\rho$  is the density of quartz ( $2.648 \text{ g cm}^{-3}$ ). In the present experiments,  $K_{AT} = -K_{BT} = 2.75 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ ,  $\tau_{AT} = 0.0338 \text{ cm}$ , and  $\tau_{BT} = 0.0510 \text{ cm}$ . Thus the mass change ( $\Delta m$ ) and the stress change ( $\Delta s$ ) of the electrode can be evaluated on the basis of the following equations which are derived from equations 2 and 3,

$$\Delta s = \frac{1}{K_{AT} - K_{BT}} \left( \frac{\tau_{AT} \Delta f_{AT}}{f_{0AT}} - \frac{\tau_{BT} \Delta f_{BT}}{f_{0BT}} \right) \quad (4)$$

$$\Delta m = \frac{\rho}{K_{AT} - K_{BT}} \left( \frac{K_{AT} \tau_{AT} \Delta f_{AT}}{f_{0AT}} - \frac{K_{BT} \tau_{BT} \Delta f_{BT}}{f_{0BT}} \right) \quad (5)$$

Resonant frequency of the AT- and BT-cut quartz crystal oscillators was monitored under galvanostatic electrolysis ( $-20.4 \mu\text{A cm}^{-2}$ ) of a  $0.2 \text{ M LiClO}_4$  aqueous solution. Figure 1 shows correlations between the frequency change ( $\Delta f$ ) and passed charge ( $\Delta Q$ ). Both dependencies are rectilinear and the BT-cut quartz crystal oscillator exhibited a larger slope than the AT-cut oscillator. This difference is attributed to a stress generated in the Pd electrode. Figure 2 depicts the correlations between the mass change (A) or the stress change (B) and the anodic charge passed, evaluated using equations 4 and 5 on the assumption that absorbed hydrogen is homogeneously distributed in the Pd electrode. As seen in the figures, both the mass change and the stress change are proportional to the passed charge. Thus the stress change is proportional to the absorbed amount of hydrogen, on the assumption that the ratio of charge consumed for proton reduction per total charge passed and the

molar ratio of hydrogen absorbed into the Pd electrode per total hydrogen generated are constant. Elongation of the interatomic spacing accompanying hydrogen uptake, which was observed by an X-ray diffraction measurement (Yamamoto *et al.*, 1990), may be responsible for the stress change. On the assumption that the number of reacting electrons is 1, apparent molecular weight of the substance which is deposited on or absorbed into the Pd is estimated as  $2.94 \text{ g mol}^{-1}$ . This value is much larger than that expected for absorption of hydrogen alone,  $1 \text{ g mol}^{-1}$ . This results indicates that the frequency change reflects not only the hydrogen absorption but also deposition of other species, change in the surface roughness, and so forth. Then the deposition of lithium is examined next.

Wagner and Gerischer (1989) described about the underpotential deposition of lithium on a gold electrode from acetonitrile solutions containing small amount of water. Here we studied on underpotential deposition of lithium in a propylene carbonate solution containing water by means of electrochemical quartz crystal microbalance technique. Cyclic voltammetric measurements were performed with the Au film-coated At-cut quartz crystal oscillator in propylene carbonate containing  $0.1 \text{ M LiClO}_4$  and  $16 \text{ mg L}^{-1}$  water. Figure 3 shows changes in the current and frequency monitored at the first potential scan. Frequency decrease was observed at potentials more negative than  $-0.6 \text{ V vs. Ag}$ ; this may reflect the underpotential deposition of lithium because the formal potential of  $\text{Li/Li}^+$  couple is  $-2.96 \text{ V vs. Ag}$ . The deposited film blocked the electrode reaction of ferrocene in the solution; this indicates that the film is not conductive. Lithium is speculated to react with water to form insulating compounds, such as lithium hydroxide or lithium hydride, immediately after the deposition. Further, there is another possibility that deposited lithium form an alloy with a substrate electrode. The underpotential deposition of lithium is anticipated to occur even in electrolyte solutions with much higher content of water, though the observation of it is interfered with the hydrogen evolution.

We have reported that a number of cracks and holes were observed on the Pd electrode surface by scanning electron microscopy after a long-time electrolysis (Yamamoto *et al.*, 1990). The increase in roughness of the electrode surface of a quartz crystal oscillator reportedly cause a change in resonant frequency (Schumacher *et al.*, 1985 and 1987). Then, contribution of respective factors, stress change, mass change (hydrogen absorption and lithium deposition), and roughness change, were estimated assuming the ratio of the charge consumed for proton reduction per total charge passed (Table 1). Thus, though some assumptions must be employed, each factor can be estimated by the present technique.

#### 4. References

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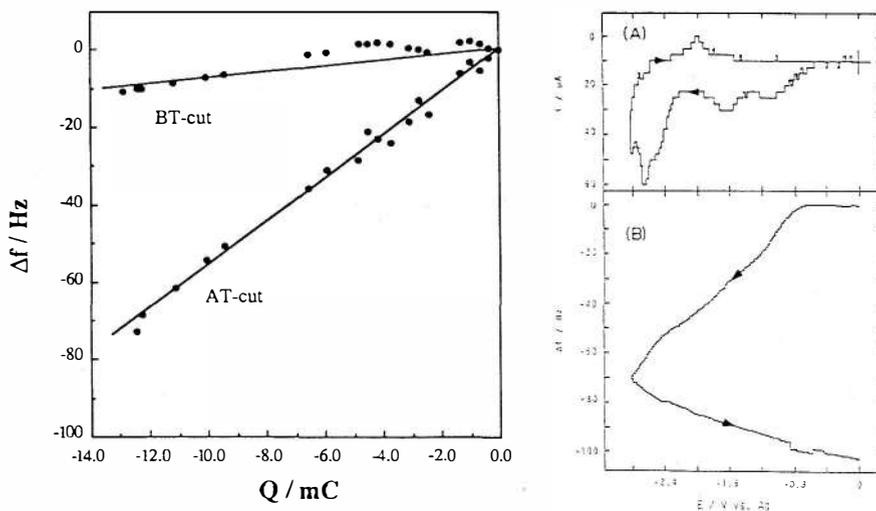


Fig. 1. Plots of the frequency change vs. the anodic charge passed for the galvanostatic electrolysis ( $-0.02 \text{ mA cm}^{-2}$ ) at Pd-coated AT-cut and BT-cut quartz crystal (5.0 MHz) in 0.2 M  $\text{LiClO}_4$  aqueous solution (pH 3.0).

Fig. 3. Cyclic voltammogram (A) and a frequency change-potential curve (B) obtained in propylene carbonate containing 0.1 M  $\text{LiClO}_4$  at the first potential scan.

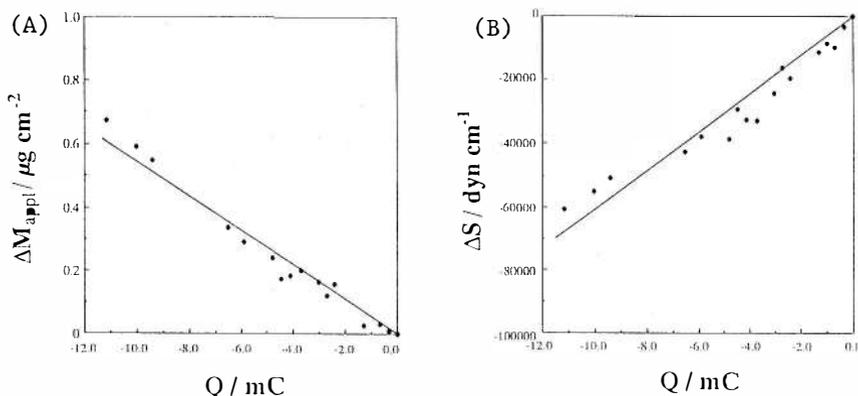


Fig. 2. Correlations between the mass change (A) or the stress change (B) and the anodic charge passed evaluated from the data shown in Fig. 1 using eqs. 4 and 5.

Table 1. Contributions of respective factors to the total frequency change.

$Q_H/(Q_H + Q_{Li})^a$	$\Delta f_{stress}$	$\Delta f_H$	$\Delta f_{Li}$	$\Delta f_{rough}$	$\Delta f_{total}$
67	1.43	0.39	1.32	0.00	3.13
90	1.43	0.52	0.40	0.77	3.13

<sup>a</sup>  $Q_H$  and  $Q_{Li}$  are charges used for reduction of  $\text{H}^+$  and  $\text{Li}^+$ , respectively.