Electrocatalytic Activity and Mechanism of Silicotungstate Modified Hg Amalgam Electrode

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Introduction

Much has been studied about the electrocatalitic activity of heteropolyanion adsorbed on a metal electrode [1]. Here we report the electro-catalytic hydrogen evolution by reductive silicotungstate ($H_4SiW_{12}O_{40}$; HPA) and the elucidation of the mechanism. This study focused reductive silicotungstate modified mercury amalgam electrode. The exchange current density for the hydrogen evolution was increased about 5^{th} orders of magnitude by the adsorption, and the *in-situ* photoelectron emission revealed that the adsorption dramatically increased the work function. These findings are well harmonized with the general trend between the work function and the exchange current density reported by Tarasati [2].

Experimental

The working electrode was the mercury amalgam electrode, which was prepared by dipping gold electrode into mercury. The reference electrode was saturated calomel electrode (SCE), and the counter electrode was a platinum wire. The silicotungstate modified mercury amalgam electrode was prepared by a continuous repetition of potential sweep between –0.4V to –1.4V in an aqueous solution containing 0.5M H_2SO_4 and 1mM of silicotungstate until appearing the stationary shape in the cyclic voltammogram.

The work function was obtained by the Fowler-Nordheim Equation of the photocurrent induced by the irradiation of an f-sec pulsed laser (780nm 100fs 82MHz 0.8W) in an electrolyte containing 0.5M H_2SO_4. The photocurrent was detected as a function of the electrode potential by lock-in detection technique with the modulated irradiation at 111Hz by a mechanical chopper.

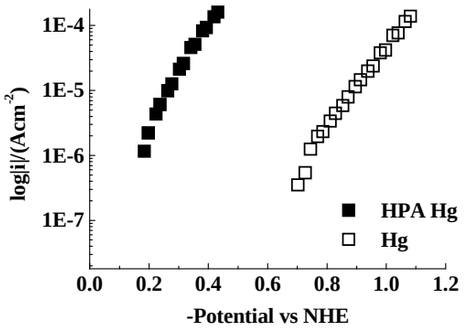

Fig. 1
Tafel plot obtained by the cyclic voltammogram. The bare Hg amalgam electrode (white square) and the HPA modified Hg amalgam electrode (black square). The hydrogen evolution exchange current estimated from this plot were 3.5×10^{-11} A/cm^2 and 3.2×10^{-6} A/cm^2. The scan rate was 100 mV/s.

Results and Discussion

The Tafel plots as shown in Figure 1 on the bare Hg amalgam electrode and the HPA modified Hg electrode indicate the exchange current 3.5×10^{-11} A/cm^2 and 3.2×10^{-6} A/cm^2, respectively. On each electrode, the hydrogen evolution current started at –1.05V |SCE| and –0.4V SCE

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The photocurrent appeared at more negative potential than –0.95V SCE and –0.35V SCE at the bare electrode and the HPA modified electrode, respectively. This big difference suggests the difference in the number of photons that induce each of the photocurrent. Fowler law can distinguish the single and double photon processes by the slopes of the logarithm of the photocurrent and the electrode potential. At the HPA modified Hg electrode, the plot of $j^{0.4}$ vs potential showed a straight line, which indicates the electron emission proceeds with a single photon. The obtained linear relationship between j0.2 and the potential demonstrates the contribution of double photons for the bare electrode as shown in Figure 2. The work function of the electrode can be calculated by the formula below;

$$I = A(nh\nu - \Phi_M - eV)^{5n/2}$$

where A, Φ_M and n are a constant, the work function and the photon number, respectively. Thus, the obtained work functions of those electrodes are 4.08 eV and 5.16 eV for the bare and the modified electrodes, respectively. The adsorption of the molecule increases the work function of the electrode. This is in accordance with the reported general trends that the hydrogen evolution current density increases as the increase of the work function of the electrode.

We will discuss more detailed analysis including with the results of QCM and SHG measurements.

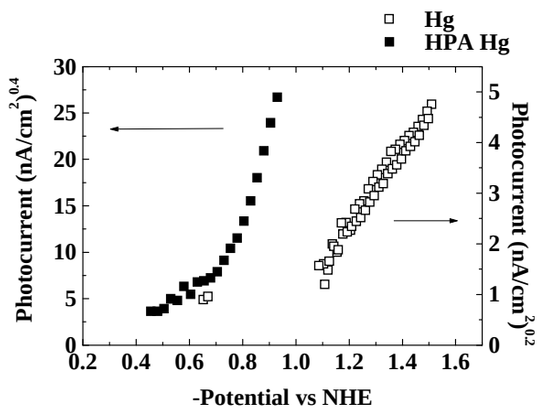

Fig. 2
Fowler plots at the HPA modified Hg electrode (black square) and the bare Hg electrode (white square), those of the plot of $j^{0.4}$ and $j^{0.2}$ vs potential were a straight line. It indicated the electron emission proceeds with a single photon and double photons. The work functions obtained by this plot of those electrodes were 5.16 eV and 4.08 eV.

[1] B.Keita,L.Nadjo, *J.Electroanal.Chem.*,**191** (1985) 441-448

[2] S.Tarasati, *J.Electroanal.Chem.*, **39** (1972) 163-184