MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012A0023 実験課題名 Title of experiment Neutron reflectometry of the adsorbed hydrogen and the oxide film on Pt polycrystalline electrode 実験責任者名 Name of principal investigator Nagahiro Hoshi 所属 Affiliation Graduate School of Engineering, Chiba University	装置責任者 Name of responsible person Norifumi Yamada 装置名 Name of Instrument/（BL No.） BL 16 実施日 Date of Experiment 11/7/2012～11/10/2012

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Pt film (100 nm) deposited on Si(111) block (36 mmφ、2 mm thick) doped with P.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

<Purpose>

Pt electrodes give redox peaks in the voltammograms before the onset potential of hydrogen evolution. These peaks have been ascribed to the adsorption and desorption of hydrogen atoms. Adsorbed hydrogen atoms affect the catalytic activity remarkably; elucidation of the nature of adsorbed hydrogen atoms is important for the understanding of the origin of electrocatalysis. However, the existence of the adsorbed hydrogen has not been verified on Pt electrodes in electrochemical environments. In this research subject, we have tried to detect the adsorbed hydrogen on Pt electrode using neutron reflectometry.

<Experimental Methods>

Si(111) is chemically polished to an atomically flat surface. Pt film (100 nm thick) is deposited on Si(111) using ion beam coater.

Electrochemical cell for neutron reflectometry was made of quartz. The design of the cell is shown in Fig. 1. Counter and reference electrodes are Pt wire. Electrolytic solution is 0.1 M $DClO_4$ in D_2O.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

In the neutron reflection measurements, the scattering length of the electrolytic solution is controlled to be the same as that of the Pt film by changing the ratio of H_2O/D_2O at hydrogen free potentials.

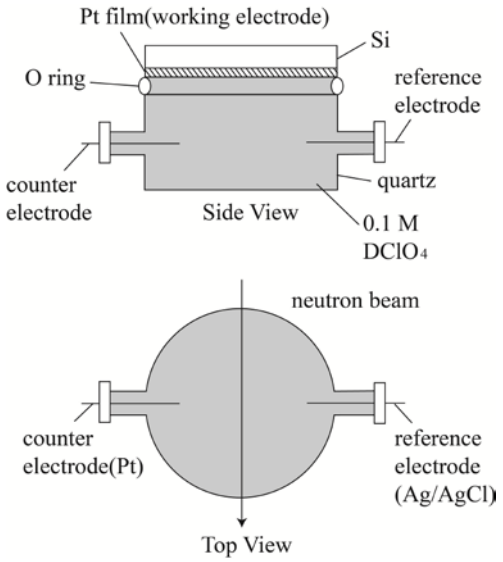

Fig. 1 Scheme of electrochemical cell for neutron reflectometry.

<Results and Discussion>

Fig. 2 shows voltammogram of Pt/Si(111) electrode in the cell for neutron reflectometry. O_2 gas in the air is dissolved in the solution. The base line of the voltammogram is tilted because the current due to the O_2 reduction reaction is overlapped with the voltammogram.

A reduction peak due to the adsorption of hydrogen ($H^+ + Pt + e^- \rightarrow$ H-Pt) is found below -0.25 V (vs Pt). An oxidation peak below -0.5 V (vs Pt) originates from the desorption of hydrogen (H-Pt $\rightarrow H^+ + Pt + e^-$). Small oxidation peak above 0 V(vs Pt) can be assigned to the formation of the oxide film (PtOH). Therefore, we measured a background data without adsorbed hydrogen at 0 V (vs Pt).

Fig. 3 shows neutron reflectometry profiles at various potentials. The profile at 0 V (vs Pt), where no hydrogen is adsorbed, gives no fringe in 0.1 M $DClO_4$ in 100% D_2O. At -0.70 and -0.80V (vs Pt) where the coverage of adsorbed hydrogen is high, the profiles are almost the same as that at 0 V (vs Pt). The profile does not change at 0.60 V(vs Pt) at which the oxide film PtOH will be formed.

We cannot detect the neutron reflectometry profile of adsorbed hydrogen in these experiments. The roughness of the Pt film prepared using ion beam coater is ±1 nm. The surface is too roughened to observe a very thin Pt-H layer. We must prepare atomically flat Pt film on Si block to measure neutron reflection of adsorbed hydrogen atoms.

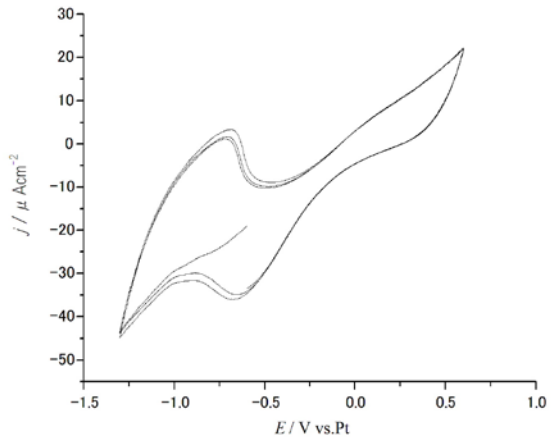

Fig. 2 Voltammogram of Pt/Si(111) in 0.1 M $DClO_4$ in 100% D_2O.

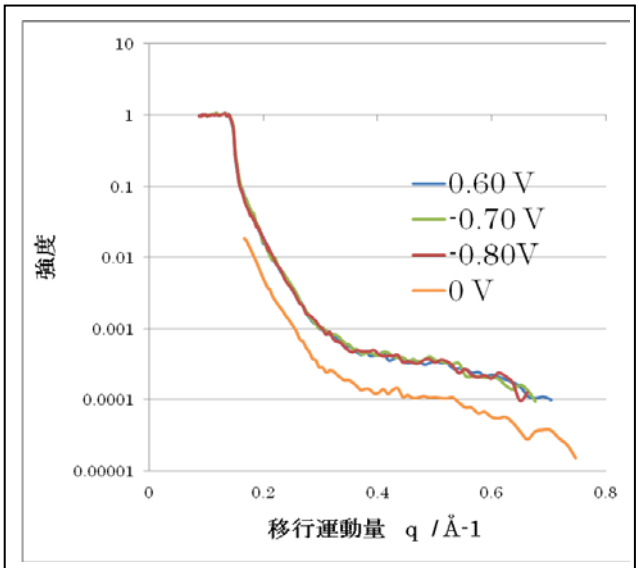

Fig. 3 Neutron reflectometry profile of Pt/Si(111) at various potentials (0.1 M $DClO_4$ in D_2O).