The effect of $Cu_xMo_6S_y$ Chevrel-phase sulfides for the electrochemical O_2 reduction on Platinum

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Polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) have attracted enormous interest as transportation application due to the high energy density and antipollution in addition to low temperature operation. In order to improve the electrochemical properties of the cathode, some semiconducting transition metal chalcogenides were proposed [1], because the chalcogenides are relatively more stable than oxides in acid medium.

In the present study, we focused Chevrel-phase sulfides, which is good electric conductor. We report the effect of $Cu_xMo_6S_y$ Chevrel-phase sulfides for the electrochemical O_2 reduction (ORR) on platinum.

$Cu_xMo_6S_y$ were prepared from the elements in an evacuated silica capsule. The capsule was heated at 1000 °C after heated at 400 °C [2]. Platinum was loaded on the Cu Chevrel phase (CuCP) by using $Pt(NH_3)_2(NO_2)_2$ ethanol solution as Pt precursor. The solution with CuCP was heated and stirred. Subsequently, the solvent was removed and the powder was heated in a flowing H_2 atmosphere to obtain the Pt deposited $Cu_xMo_6S_y$ catalyst powder. In this work, we studied the ORR kinetics of the prepared catalysts by using a thin-film rotating ring-disk electrode. Kinetically controlled current, I_k, was obtained with Koutecky-Levich plots by extrapolating the regression lines on the plots to the y intercept. The kinetically controlled current density, J_k, was calculated by dividing I_k with the real surface area of the electrode determined by electric charge required for the hydrogen adsorption/desorption on a polycrystalline Pt surface, i.e., 210 μ C/real cm^2 [3].

J_k is larger than that of pure Pt and, furthermore, indicated that J_k increase with the decrease of Cu composition. In order to clarify these results, we used synchrotron X-ray absorption method to evaluate the electronic and local structure around Pt.

For measure of Pt electronic structure, the L_3 and L_2 edge XANES can provide significant information on the d-band vacancies. The edge areas calculated by numerical integration using Simpson's rule show the information [4]. Figure 1 shows the results. This analysis indicated that Pt d-band vacancies increase with decreasing Cu compositions. Figure 2 shows Fourier transforms of the EXAFS at the Pt L_3 edge for $Pt/Cu_xMo_6S_y$. Pt-Pt bond distances for $Pt/Cu_xMo_6S_y$ are clearly shorter than pure Pt and Pt/Vulcan. These results (increase of Pt d-band vacancies and shorter Pt-Pt bond distance) favor high ORR [4].

The results in figure 1 and figure 2 indicate that Pt particles deposited on $Cu_xMo_6S_y$ lose their valence electrons. This result indicates the lost electrons could transfer to $Cu_xMo_6S_y$. To clear this point, we measured Mo L_3 edge XANES spectra of $Pt/Cu_xMo_6S_y$. Figure 3 shows the white line of Mo L_3 edge intensity decreased after Pt deposited. These results indicate Mo in $Cu_xMo_6S_y$ compensated the lost electrons of Pt. The lost electrons supposedly transfer to the covalent band made by Mo and S in Cu Chevrel phase from Pt. Increase of Cu compositions may lead to increase of electrons in the

band. Accordingly, lower Cu compositions favor to receive the electrons from Pt into the band and increase more the d-band vacancy of Pt. Consequently, lower Cu compositions lead to higher J_k.

References
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[2] S. Yamamoto et al. Mat. Res. Bull., 18, 1311(1983)
[3] T.Toda et al.,J. Electrochem. Soc., 146,3750(1999)
[4] S.Muerjee et al.,J. Electrochem. Soc., 142,1409(1995)
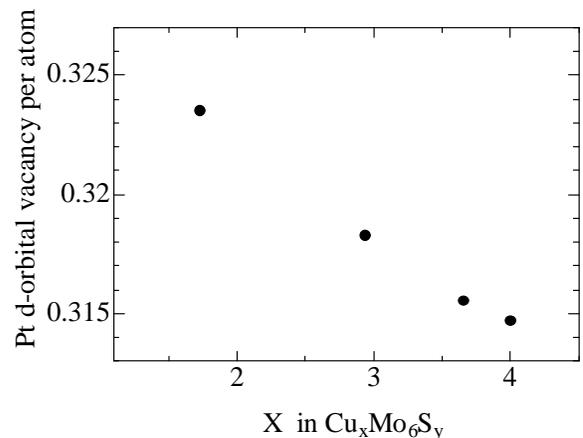
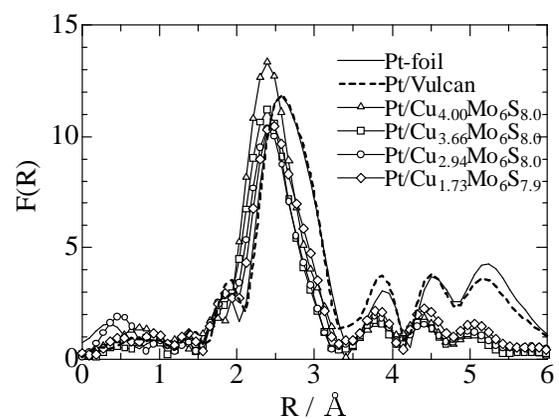Fig. 1 The d-band vacancies derived from an analysis of the Pt L_3 and L_2 white lines.

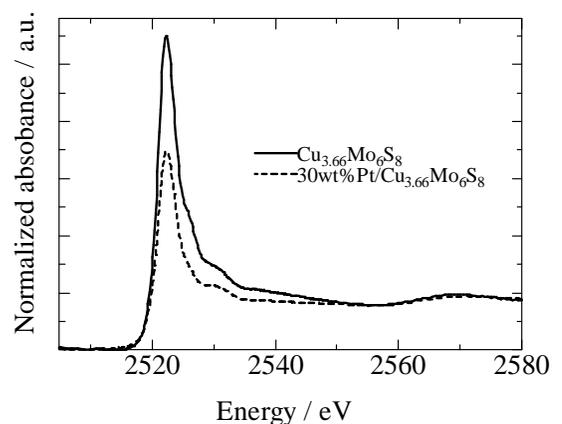Fig.2 Pt L_3 edge Fourier transforms of Pt / $Cu_xMo_6S_y$

Fig.3 Mo L_3 edge XANES spectra of $Pt/Cu_{3.66}Mo_6S_8$ and $Cu_{3.66}Mo_6S_8$