# Reaction of Tungsten Metal Powder with Hydrogen Peroxide to Form Peroxo Tungstates, An Useful Precursor of Proton Conductor

Hitoshi Nakajima, Tetsuichi Kudo, and Noritaka Mizuno†
*Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106*
†*Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The title reaction was investigated by $^{183}$W NMR, Raman and TOF-MASS spectroscopy. Peroxotungstates with peroxo/W = 2 and peroxo/W = 1 were formed. The latter compounds are previously unknown. The removal of hydrogen peroxide from the reaction solution by the decomposition with Pt net promoted the polymerization of these species.

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The reaction of tungsten metal with a hydrogen peroxide in an aqueous solution formed an unknown amorphous peroxopolytungstate.[1] The peroxopolytungstate has attracted much attention because of its high applicability to precursors of proton conductor,[2] photoresist,[3] and electrochromic device.[2,4] It is also interesting that a metastable hexagonal tungsten trioxide is formed by the calcination.[5] Therefore, it is important how the reaction of tungsten metal with hydrogen peroxide proceeds for the precise control. However, little is known of the reaction.[6,7]

Here we wish to investigate the reaction of tungsten metal with hydrogen peroxide with $^{183}$W NMR, Raman, and TOF-MASS spectroscopy.

The peroxopolytungstate was prepared by the reaction of tungsten metal powder (Mitsuwa Chemical Co. Ltd., particle size ca. 1 μm) with 30% aqueous hydrogen peroxide (Junsei Chemical Co. Ltd.) as follows: 11 g of tungsten powder was suspended in 25 ml water, and then 25 ml of 30 wt% hydrogen peroxide was added in a single step without stirring. The reaction started immediately. After 15 min, 20 ml of 30 wt% hydrogen peroxide was further added. While the solution was kept at room temperature for 24 h, it was sampled after 1 and 24 h from the start of the reaction. And then it was filtered to remove unreacted tungsten metal and Pt net, which was activated by hydrogen hexachloroplatinate, was put into the clear solution to decompose an excess amount of unreacted hydrogen peroxide. Again the solution was filtered and sampled, and evaporated to dryness at 35 ℃. Resulting powder was amorphous by XRD.

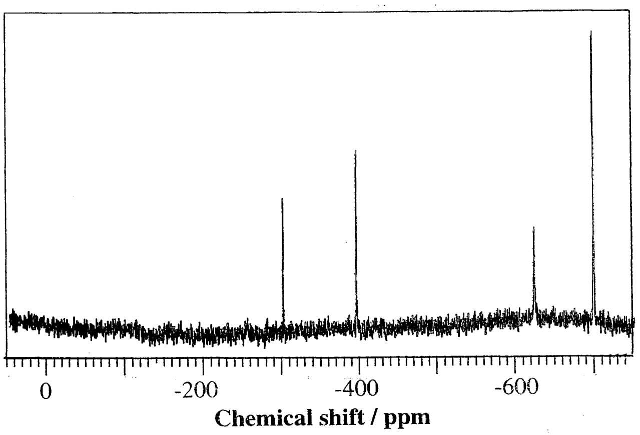

Figure 1. $^{183}$W NMR spectrum of the reaction solution of tungsten metal with hydrogen peroxide after 1 h.

$^{183}$W NMR spectra were recorded at a frequency of 11.2 MHz using a JEOL GX270 FT spectrometer referenced to a 2M $Na_2WO_4$ in $D_2O$ solution. Raman spectra were measured with T-64000 (JOBIN YVON). TOF-MASS spectrum was measured with KOMPACT MALDI IV (Shimadzu).

$^{183}$W NMR spectrum of the reaction solution after 1 h is shown in Figure 1. Four signals were observed at -697, -621, -392, and -300 ppm. The spectrum after 24 h also showed the same peaks with a similar intensity ratio, showing that the tungsten species are not changed with time. The signal at -697 ppm is probably assigned to $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ according to Reference 8. Ghiron *et al.* have prepared the solution containing $[WO_2(O_2)_2]^{2-}$ and $[WO(O_2)_2(OH)]^{-}$ as well

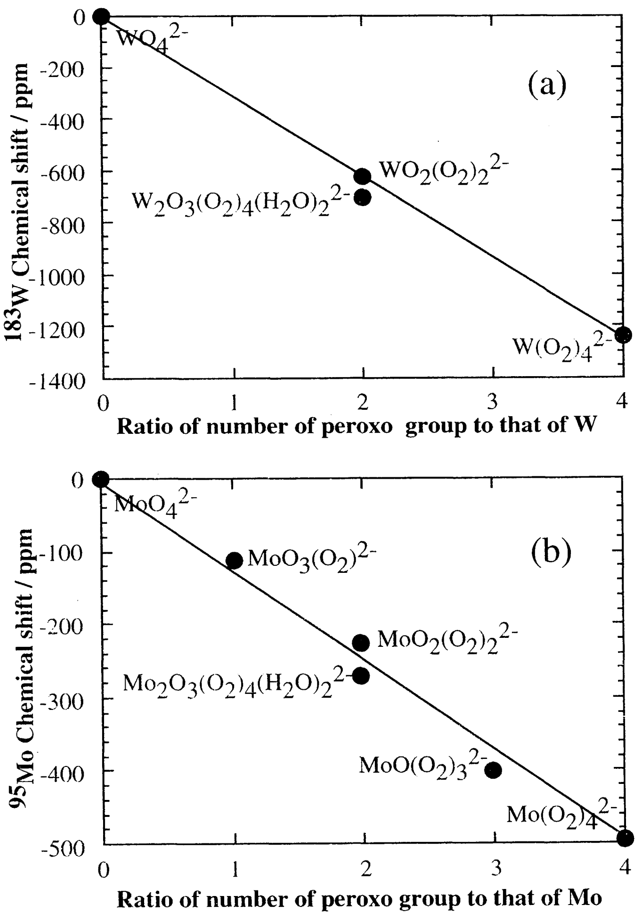

Figure 2. $^{183}$W and $^{95}$Mo chemical shifts. (a) peroxo tungsten complexes (b) peroxo molybdenum complexes (Cited from Refeerence 10).

as $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and confirmed their presence by UV.[9] In the same way as Ghiron, the solution was prepared and the $^{183}$W NMR spectrum was measured. The spectrum showed two signals at -699 and -637 ppm. The former signal is assigned to $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ as described. The latter signal was shifted to lower field by decreasing pH of the solution, i. e. by the protonation. It was confirmed -637 ppm was shifted to -657 ppm increasing pH to 2.0. Therefore, the signal at -621 ppm is likely assigned to $[WO_2(O_2)_2]^{2-}$, $[WO(O_2)_2(OH)]^{-}$ and/or the protonated species.

Next, the signals at -392 and -300 ppm were investigated. Figure 2a shows the correlation between $^{183}$W chemical shifts and ratios of number of peroxo group to that of W for various peroxoisopolytungstates. A good correlation was observed. A similar linear correlation can be pointed out for peroxo compounds of Mo (Figure 2b).[10] It was reported for molybdenum that strong $\sigma$ donors such as peroxo group produce upfield shifts.[8, 11] Therefore, the fact that the four signals observed in Figure 1 lie upfield of that of $WO_4^{2-}$ is due to the coordination of peroxo groups to tungsten atom. In addition, the linear correlation was observed in Figure 2a as well as in Figure 2b. These facts suggest that the signals at -392 and -300 ppm are assignable to peroxotungstates with $O_2^{2-}$ /W = 1. The chemical shift of dimer species were by ca. 50 - 80 ppm higher field than those of monomer species in the case of peroxo complexes with $O_2^{2-}$ / M = 2 (M = W, Mo) shown in Figures 2a and 2b. This fact suggests that the signal at -392 ppm is assigned to a dimer species and that at -300 ppm to a monomer species.

Raman data support the idea: The Raman spectrum of the reaction solution after 1 h showed the bands at 561, 610, 854, 877, and 966 cm$^{-1}$ (Figure 3a). The 877 cm$^{-1}$ band is due to free $H_2O_2$. The bands at 561, 610, 854, and 966 cm$^{-1}$ can be assigned to $\nu_{as}(W(O_2))$, $\nu_s(W(O_2))$, $\nu$(O-O), and $\nu$(W=O), respectively, according to Reference 8. The bands around 700 cm$^{-1}$, which are assigned to $\nu$(O-W-O), were not observed, indicating that W species in the reaction solution are not polymerized and almost mono- and dinuclear peroxotungstates.

The removal of unreacted hydrogen peroxide from the reaction solution with Pt net resulted in the appearance of 695 cm$^{-1}$ band accompanied by the disappearance of 610 and 854 cm$^{-1}$ bands (Figures 3a and 3b). The 695 cm$^{-1}$ band has been assigned to $\nu$(O-W-O).[12] This shows the polymerization of mono- or dinuclear peroxotungstates. The negative TOF-MASS spectrum showed a signal at m/e = -2852 in the m/e range of -1500 to -4000, indicating the presence of polytungstate. The full characterization and crystallization of this polytungstate are in progress. When a small amount of $H_2O_2$ was used, the precipitate of $WO_3\cdot H_2O$ was observed, showing the higher extent of the polymerization. In contrast, in the present reaction conditions, reproducible results and no precipitation were obtained. The polymerization of Nb-containing polyanions with the disappearance of $H_2O_2$ was also observed.[13, 14]

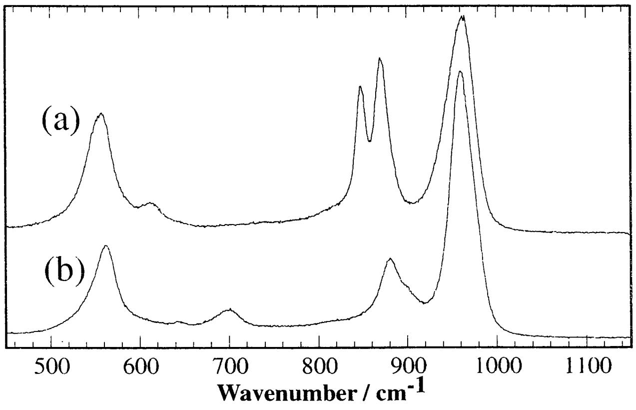

**Figure 3.** Raman spectra of the reaction solution of tungsten metal with hydrogen peroxide. (a) After 1 h, and (b) After the decomposition of unreacted hydrogen peroxide with Pt net.

The polymerized polytungstate prepared in this way provides homogeneous thin film and shows relative high protonic conductivity (ca. $1 \times 10^{-3}$ S cm$^{-1}$ at 25 ℃).[15, 16] In addition, the conductivity did not much change with the humidity in contrast with the greater change for $H_3PW_{12}O_{40}\cdot 29H_2O$.[17] The characteristic is important for the application to the proton conductor.

In conclusion, mono- and dinuclear peroxotungstates with peroxo/W ratios of 1, which were previously unknown, and 2 are formed by the reaction of tungsten metal with hydrogen peroxide. The removal of hydrogen peroxide promoted the polymerization and the polymerized polytungstate showed good characteristics as a proton conductor.

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## References

1 T. Kudo, H. Okamoto, K. Matsumoto, and Y. Sasaki, *Inorg. Chim. Acta*, **111**, L27 (1986).
2 H. Okamoto, K. Yamanaka, and T. Kudo, *Mater. Res. Bull.*, **21**, 551 (1986).
3 T. Kudo, A. Ishikawa, H. Okamoto, K. Miyauchi, F. Murai, K. Mochiji, and H. Umezaki, *J. Electrochem. Soc.*, **134**, 2607 (1987).
4 T. Kudo, S. Takano, A. Kishimoto, and Y. Aikawa, *Denki Kagaku*, **59**, 718 (1991).
5 J. Oi, A. Kishimoto, T. Kudo, and M. Hiratani, *J. Solid State Chem.*, **96**, 13 (1992).
6 K. Matsumoto, Y. Ozawa, Y. Sasaki, T. Kudo, and H. Okamoto, *Inorg. Chim. Acta*, **159**, 185 (1989).
7 M. Hashimoto, T. Ozeki, H. Ichida, Y. Sasaki, K. Matsumoto, and T. Kudo, *Chem. Lett.*, **1987**, 1873.
8 N. J. Campbell, A. C. Dengel, C. J. Edwards, and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, **1989**, 1203.
9 A. F. Ghiron and R. C. Thompson, *Inorg. Chem.*, **27**, 4766 (1988).
10 V. Nardello, J. Marko, G. Vermeersch, and J. M. Aubry, *Inorg. Chem.*, **34**, 4950 (1995).
11 B. Piggott, S. F. Wong, and D. J. Williams, *Inorg. Chim. Acta*, **141**, 275 (1988).
12 F. Daniel, B. Desbat, J. C. Lassegues, B. Gerans, and M. Figlarz, *J. Solid State Chem.*, **67**, 235 (1987).
13 R. G. Finke and M. W. Droege, *J. Am. Chem. Soc.*, **106**, 7274 (1984).
14 V. W. Day, W. G. Klemperer, and C. Schwartz, *J. Am. Chem. Soc.*, **109**, 6030 (1987).
15 Presented at the 1996-Fall Meeting of the Electrochemical Society of Japan, Kusatsu, 1996, Abstr., 142.
16 To be presented at the 192nd ECS/ISE Joint Meeting, Paris, 1997.
17 O. Nakamura, T. Kodama, I. Ogino, and Y. Miyake, *Chem. Lett.*, **1979**, 17.