A self-healing phenomenon of thin δ-MnO$_2$ film in the oxidative decomposition of hydrogen peroxide

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Everybody knows the fact that bulk MnO$_2$ catalyzes oxidative decomposition of aqueous H$_2$O$_2$. Its mechanism can be described as follows, according to the literature [1]:

$$MnO_2 + H_2O_2 + 2H^+ \leftrightarrows Mn^{2+} + 2H_2O + O_2$$
$$K = 4 \times 10^{20} \tag{1}$$

$$Mn^{2+} + H_2O_2 \leftrightarrows MnO_2 + 2H^+$$
$$K = 1.3 \times 10^{16} \tag{2}$$
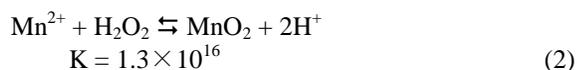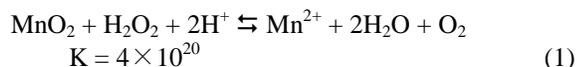
It should be noted that the catalytic cycle is maintained only when sufficient amounts of MnO$_2$ and H$_2$O$_2$ are involved. In other words, it is difficult to remove a small amount of H$_2$O$_2$ completely using a thin film of MnO$_2$, avoiding its leaching. In this work, we have focused on the leaching of δ-MnO$_2$ film during oxidative decomposition of H$_2$O$_2$. When a constant potential of +0.8 V was applied, a self-healing phenomenon of the film was found as a result; that is, the δ-MnO$_2$ film reacts with H$_2$O$_2$ to be reduced to soluble Mn^{2+} ions which are oxidized at +0.8 V, returning to MnO$_2$ film where the reaction with H$_2$O$_2$ is resumed.

An aqueous solution of 2 mM KMnO$_4$ was used as the deposition bath. A constant potential of 0 V vs Ag/AgCl was applied to an ITO glass electrode to deposit thin film of MnO$_2$. In this condition, low-crystalline birnessite (δ-MnO$_2$) can be created [2]. The ITO-supported MnO$_2$ film was immersed into a 0.5 M Na$_2$SO$_4$ solution containing 2 mM H$_2$O$_2$ and held at open-circuit potential (+0.15), +0.4, + 0.6, +0.8, and +1.0 V. A glassy carbon disk, which is inactive toward H$_2$O$_2$, was used as the counter electrode. Concentration of residual H$_2$O$_2$ was evaluated as a function of time according to the phenolphthalin method. On the other hand, *in situ* UV-vis spectra were acquired in a quartz cuvette filled with the same solution. The MnO$_2$/ITO working electrode was located perpendicular to the light beam while small counter and reference electrodes were placed outside of the beam.

Figure 1 shows time course of absorption spectra due to phenolphthalein (red) which had been generated by the oxidation of phenolphthalin (colorless) with H$_2$O$_2$, taken at an applied potential of +0.8 V. The absorbance at λ = 552 nm was depicted in the inset, which was normalized to the initial value. Concentration of residual H$_2$O$_2$ (A/A$_o$) decreased immediately after immersion and reached nearly 0 in 24 h, meaning the complete loss. One should note the slowing down of the absorbance decrease in the region from 90 to 400 min. *In situ* absorption spectra of the MnO$_2$ film on an ITO substrate were recorded under the same conditions as the above. Broad absorption with no distinct peaks appear between 300 and 700 nm, which can be ascribed to *d-d** transition of the Mn^{4+} state (t$_{2g}^3$e$_g^0$). The inset indicates the time course of the normalized absorbance (A/A$_o$) at 380 nm. The absorption decreased in intensity immediately after starting the measurement, due to the leaching of MnO$_2$

film as a result of the reduction to soluble Mn^{2+} with H$_2$O$_2$. Interestingly, the absorbance increased from 90 min to reach almost its original value. As shown in Figure 3, the film obtained after polarization at +0.8 V with H$_2$O$_2$ exhibited more intense diffraction peak at 12° in 2θ than the as-deposited film. Since this peak can be assigned to δ-MnO$_2$, it is reasonable to assume that Mn^{2+} ions generated as a result of the reaction between MnO$_2$ and H$_2$O$_2$ are oxidized at +0.8 V in the presence of Na$^+$ ions, depositing again on the surface of ITO electrode with the same crystalline structure. At an applied potential of +0.9 V, the MnO$_2$ film remained unchanged during the reaction with H$_2$O$_2$, while H$_2$O$_2$ was decomposed completely. Here, the generated Mn^{2+} ions can be rapidly reoxidized before leaching.
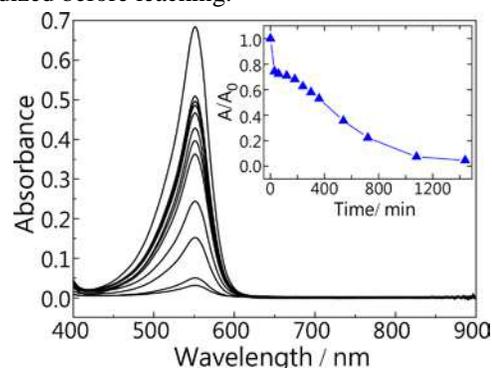
Fig. 1 Time course of absorption spectra taken by the phenolphthalin method to determine the residual amount of H$_2$O$_2$. Polarization was made at +0.8 V in a 0.5 M Na$_2$SO$_4$ solution with 2 mM H$_2$O$_2$.
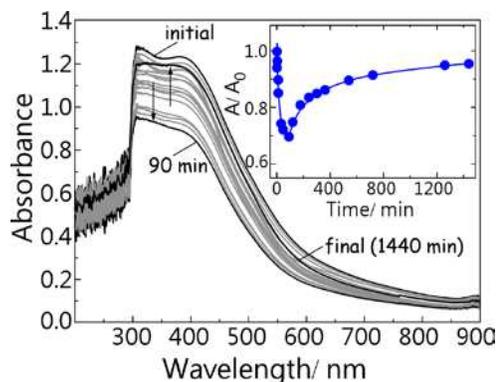
Fig. 2 *In situ* absorption spectra of δ-MnO$_2$ film obtained in a 0.5 M Na$_2$SO$_4$ solution with 2 mM H$_2$O$_2$ at an applied potential of +0.8 V.
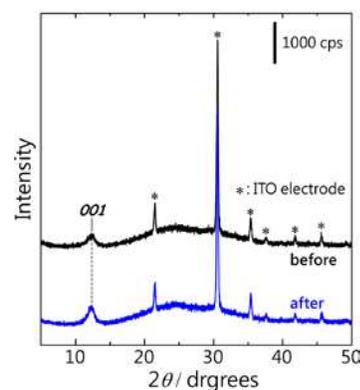
Fig. 3 XRD patterns of the δ-MnO$_2$ film before and after polarization at +0.8 V in a 0.5 M Na$_2$SO$_4$ solution with 2 mM H$_2$O$_2$.

References
[1] Broughton and Wentworth, *J. Am. Chem. Soc.*, **69**, 741 (1947).
[2] Nakayama *et al.*, *J. Electrochem. Soc.* **159**, A1176 (2012).