# Cathodic Oxidation of Sulfoxides to Sulfones Using a Tungstate/Pertungstate Redox Mediator

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A new cathodic oxidation system for the oxidation of sulfoxides was developed. The system involves the cathodic reduction of dioxygen to hydrogen peroxide which oxidizes tungstate to pertungstate in the solution, and sulfoxides are oxidized to the corresponding sulfones with the resulting tungstate/ pertungstate redox mediator in high effiency and selectivity

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Paired electrosynthesis, which utilizes purposively both of cathodic and anodic reactions, should be important from a practical aspect and has received much interest as an efficient electrochemical process in recent years.[1,2] Among various types of the paired electrosynthesis, a process for forming the same product from the same starting compound at the cathode and anode can give efficiency higher than 100%, and also is the simplest and most practical from an industrial aspect. For this type of process, either cathodic oxidation or anodic reduction must be developed.

From the above point of view, some cathodic oxidation systems have been proposed so far, and a few of them have been attempted to combine with the conjugated anodic oxidation for realizing the paired electrosynthesis. In general, oxygen species such as hydrogen peroxide ($H_2O_2$) and superoxide ion ($O_2^{\cdot -}$) generated by the cathodic reduction of dioxygen have been used as oxidizing reagents for the cathodic oxidation. The most typical one is $H_2O_2$. However, its reactivity is not high when generated in the cathodic solution. Therefore, the cathodically-generated $H_2O_2$ is used converting into OH radical (So-called electrogenerated Fenton's reagent) with a higher reactivity in the presence of metal ions such as $Fe^{2+}$, $Cu^{+}$, $V^{4+}$ and $Mn^{3+}$.[3-12] A superoxide ion ($O_2^{\cdot -}$) cathodically-generated in non-aqueous solvents is also a reactive oxidant.[13] However, though these oxygen radical species have unique reactivities in the direct introduction of oxygen atoms to the starting compound molecules, they sometimes result in low reaction selectivity due to their extremely strong reactivities.

From the above consideration, we aimed to explore a possible ionic oxidant species which can act as a redox oxidation mediator derived from cathodically-generated $H_2O_2$. After trials and errors, a tungstate/pertungstate redox couple could be found as a purposive mediatory system. In this paper, it is demonstrated that this couple can act as the mediator for the efficient and selective cathodic oxidation of sulfoxides to the corresponding sulfones.

For electrolysis, an H-type divided cell equipped with a polycrystalline graphite cathode (12 $cm^2$) and a platinum anode was used. The catholyte was a solution (60 $cm^3$) containing sulfoxide (17 mM; 1 M= 1 mol $dm^{-3}$), $Na_2WO_4$ (2 mM) and $KH_2PO_4$ (100 mM), and was electrolyzed galvanostatically at 1 mA $cm^{-2}$ of current density by passing 2 F(1 F= 96480 C) $mol^{-1}$ (Sulfoxide base). The pH of the catholyte was adjusted by adding 5 M HCl. An oxygen gas stream (50 $cm^3$ $min^{-1}$) was introduced into the catholyte during the electrolysis. The products and unreacted sulfoxides were analyzed by HPLC(S-$C_{18}$ column). An analytical material balance in each experiment was higher than 95%.

Figure 1 demonstrates a general reaction scheme for the cathodic oxidation of sulfoxides to sulfones.

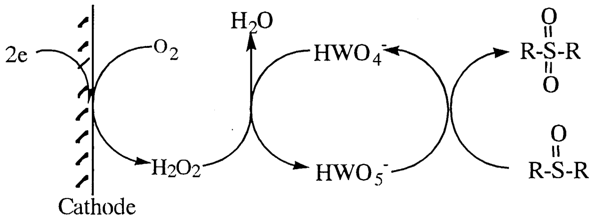

**Figure 1.** Reaction scheme for the cathodic oxidation of sulfoxides to sulfones.

As shown in Figure 2, the current efficiency for the cathodic oxidation of dimethyl sulfoxide (Selected as a model starting compound) has a maximum at pH 5. At pH's lower than 5, the pertungstate is formed as $H_2WO_5$ which easily polymerizes to lead polypertungstate.[14,15] On the other hand, the pertungstates exist as $WO_5^{2-}$ at high pH and $HWO_5^-$ at pH 5.[16] Among the pertungstates, $HWO_5^-$ has the strongest oxidizing power. This is a reason for the maximum current efficiency at pH 5.

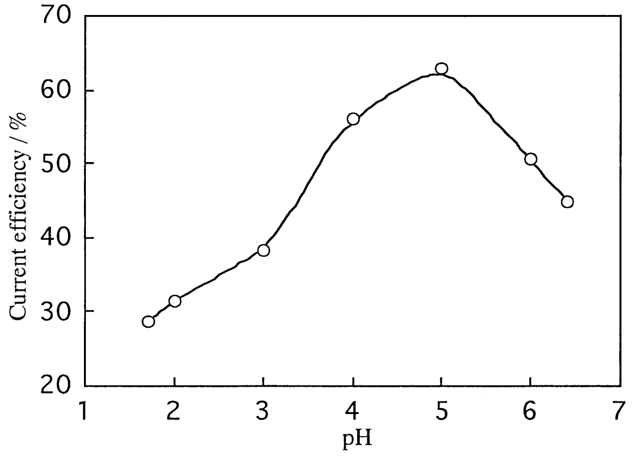

**Figure 2.** Effect of pH on current efficiency for the cathodic oxidation of dimethyl sulfoxide at 50 °C.

Figure 3 shows effect of temperature on the current efficiency. Its maximum was obtained at 50 °C. It was experimentally confirmed in this work that the efficiency (76% at pH 5 and 50 °C) for the generation of $H_2O_2$ increases with a decrease in temperature, while the formation and reaction rates of $HWO_5^-$ decreases. As a result, the overall efficiency was observed to have the maximum.

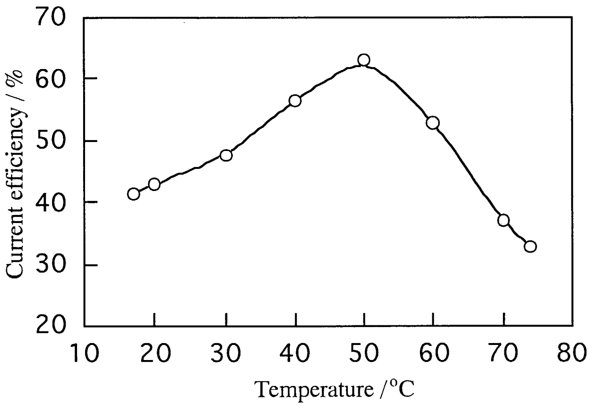

**Figure 3**. Effect of temperature on current efficiency for the cathodic oxidation of dimethyl sulfoxide at pH 5.

Typical results of the cathodic oxidation of sulfoxides are shown in Table 1. No by-product was formed. It is noticeable that the alcoholic OH groups of the starting $(HOCH_2CH_2)_2SO$ are not oxidized at 2 F $mol^{-1}$ of charge passed, since alcohols can be oxidized with pertungstates in general.[17] Similarly, sulfides could be selectively oxidized to the corresponding sulfoxides without the sulfones at 2 F $mol^{-1}$. For instance, the oxidation of $(HOCH_2CH_2)_2S$ and $(HOOCCH_2)_2S$ gave the corresponding sulfoxides in 75 and 73% of current efficiencies, respectively, which were higher than those obtained without $Na_2WO_4$.These facts suggest a possibility for product-selectivity control by adjusting amount of charge passed.The turnover number of the tungstate mediator was more than 20. Dimethyl sulfoxide was not oxidized in the absence of $Na_2WO_4$.

**Table 1**. Cathodic oxidation of sulfoxides to sulfones[a]

| Sulfoxide | Current efficiency / % |
|---|---|
| $(CH_3)_2SO$ | 71 |
| $(HOCH_2CH_2)_2SO$ | 67 |
| $(HOOCCH_2CH_2)_2SO$ | 64 |

[a] Current density, 0.5 mA $cm^{-2}$; concentration of $Na_2WO_4$, 1mM.

This type of electrochemical reaction should be controlled by a variety of electrolytic conditions other than pH and temperature. It is known that not only tungstates but also peroxy compounds of other metals can oxidize a variety of organic compounds other than sulfoxides.[17-27] Further investigations such as the optimization and extention of reactions are in progress.

To Professor Hans Schäfer this paper is dedicated on the occasion of his 60th. birthday.

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