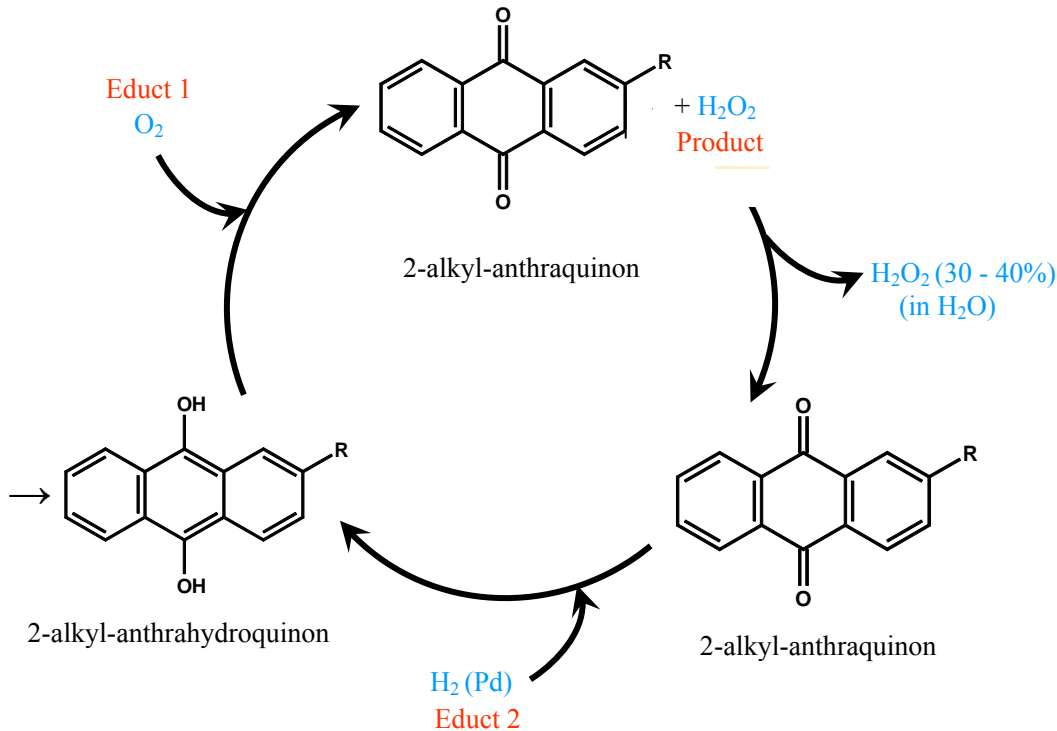


## 1. H<sub>2</sub>O<sub>2</sub> Formation “State of the Art”

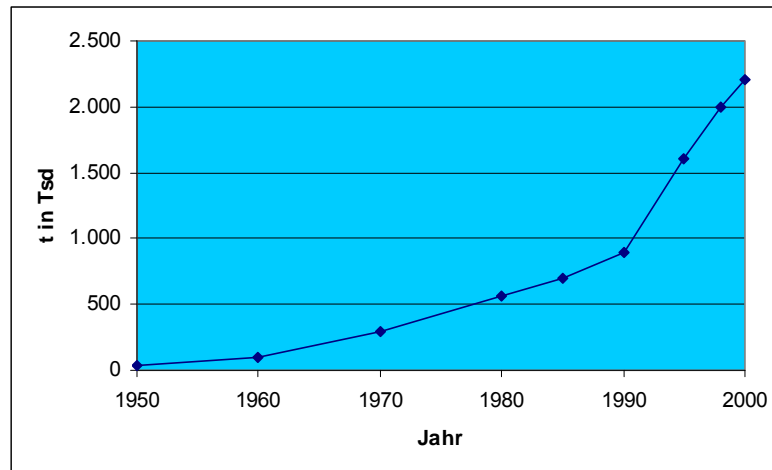
### 1.1. Industrial Synthesis

The standard process for the industrial production of H<sub>2</sub>O<sub>2</sub> solutions is the so called “anthraquinon process”, which relies on the reversible oxidation of the organic compound anthraquinon, whereby mostly alkyl derivatives of anthraquinon, e.g. 2-ethyl-anthraquinon, are employed. The process is displayed in the following graph.



**Fig. 1:** Catalytic cycle for the formation of H<sub>2</sub>O<sub>2</sub> via 2-alkyl-anthraquinon.

The process was developed by Degussa decades ago and accounts for 95 % of the annual global production of H<sub>2</sub>O<sub>2</sub>. Nowadays, the worldwide production volume of H<sub>2</sub>O<sub>2</sub> is about 2.200.000 tons, whereby the production volume and market demand is steadily growing, since the beginning of industrial H<sub>2</sub>O<sub>2</sub> production in the 50ties [1; 2].

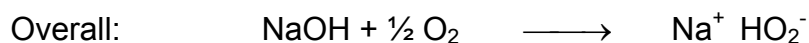
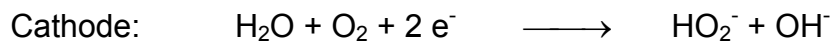


**Fig. 2:** World production volume of H<sub>2</sub>O<sub>2</sub> between 1950 and 2000.

The main application areas of H<sub>2</sub>O<sub>2</sub> are the synthesis of sodium perborate and sodium percarbonate for washing and dishwasher detergents and bleaching of (recycled) paper. A minor application is the treatment of drinking and waste water. For all of these application areas, aqueous solutions of H<sub>2</sub>O<sub>2</sub> with a high H<sub>2</sub>O<sub>2</sub> concentration are required.

## 1.2 Electrochemical Synthesis

Another way to synthesize H<sub>2</sub>O<sub>2</sub> employs a diluted NaOH-solution which undergoes electrolysis [7]. The following equations describe the electrochemical process:



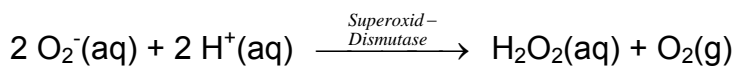
The process is carried out in an electrochemical cell with carbon black coated graphite electrodes and oxygen under atmospheric pressure (Dow process). It delivers alkaline peroxide with a NaOH/H<sub>2</sub>O<sub>2</sub>-weight ratio of approx. 1.7:1. If the electrochemical cell is driven with 2.3 V and 62 mA/cm<sup>2</sup> the electricity yield sums up to 90%, by additionally applying an ion exchange membrane this value increases to 95% and the process yields in a solution of 2.1% (w/w) of HO<sub>2</sub><sup>-</sup> in a solution of 5 % (w/w) of NaOH. The described alkali peroxide technology is appropriate to applications where it is not necessary to separate NaOH from the peroxide, like in pulp bleaching processes. Another paper reports on a recently developed electrochemical membrane cell that employs sulphuric acid as electrolyte and uses poly(4-vinylpyridinium-p-toluolsulphonate) (PVPPTS) to increase the output of the cell in terms of peroxide concentration by enhancing the current density and reducing the cell voltage [2].

The group of I. Yamanaka (Tokyo Institute of Technology, Japan) is working on the synthesis of H<sub>2</sub>O<sub>2</sub> in fuel cells by the reaction of oxygen and hydrogen. An oxygen excess in this kind of electrochemical cells leads to the formation of H<sub>2</sub>O<sub>2</sub> and generates even electricity. It was even possible to produce neutral aqueous H<sub>2</sub>O<sub>2</sub> solutions (up to 8 wt-%) from O<sub>2</sub> and water by using a cell with a solid polymer

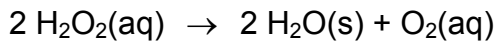
electrolyte exposed to an oxygen stream (or just even to air). The cathode was made by hot pressing of a blend of activated carbon oxidized by HNO<sub>3</sub>, Teflon powder, and vapor grown carbon fiber coated with Nafion to ensure the neutrality of the product [3].

### 1.3 Formation in Living Systems

The formation of H<sub>2</sub>O<sub>2</sub> in organisms can occur at the end of the respiratory chain, since at this point of the metabolism, a side-reaction, viz. the reduction of O<sub>2</sub> results in the formation of the superoxide anion radical O<sub>2</sub><sup>-</sup>, which is highly toxic. This radical is removed from the cell by the enzyme superoxide dismutase (SOD), which comprises one or two transition metal ions in the active site. Dependent on the species, the transition metal ions involved are Mn<sup>3+</sup>, Fe<sup>3+</sup>, or Cu<sup>2+</sup> and Zn<sup>2+</sup>.



Since H<sub>2</sub>O<sub>2</sub> is also toxic for the cell, all types of biological species take care of the rapid decomposition of H<sub>2</sub>O<sub>2</sub> in the cells by the enzyme catalase, which cleaves H<sub>2</sub>O<sub>2</sub> according to the following equation:

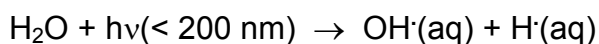


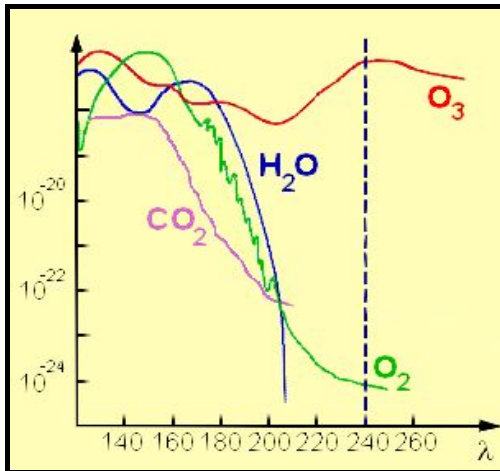
## 2. Novel Catalytic Processes

A rather novel way for the industrial production of H<sub>2</sub>O<sub>2</sub> relies on a catalytic process in methanol solution, which was developed by Degussa and Headwaters recently [1]. This process involves the direct synthesis of hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (DSHP process) from H<sub>2</sub> and O<sub>2</sub>, which is feasible on a heterogeneous catalyst [4]. The essential part of the process is the so-called N<sub>x</sub>Cat<sup>TM</sup> catalyst, which comprises Pd or Pt nanoscale particles activated by iodine. Due to the explosive character of hydrogen/oxygen blends, the process requires extended safety measures.

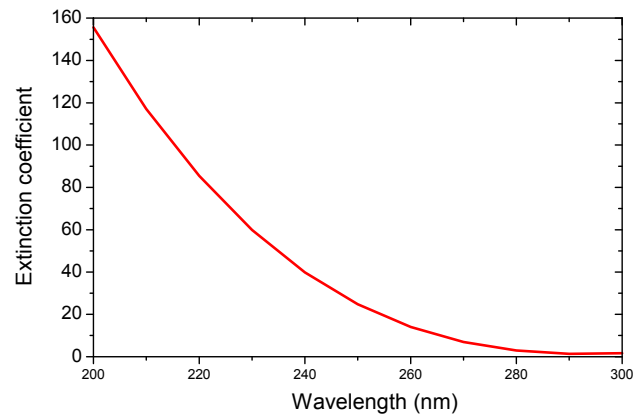
## 3. Photo Catalytic Formation of H<sub>2</sub>O<sub>2</sub>

If water is irradiated by UV radiation with a wavelength below 200 nm, the cleavage of the O-H bond is observed, which results in the formation of hydroxyl and H<sup>•</sup> radicals.





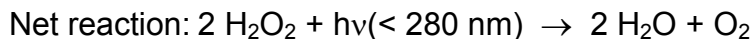
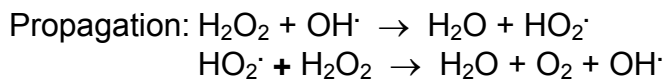
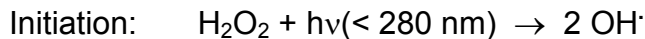
**Fig. 3:** Absorption spectra of  $H_2O$ ,  $O_2$ ,  $O_3$ , and  $CO_2$  in the UV-C and VUV range.



**Fig. 4:** Absorption spectrum of  $H_2O_2$  in  $H_2O$ .

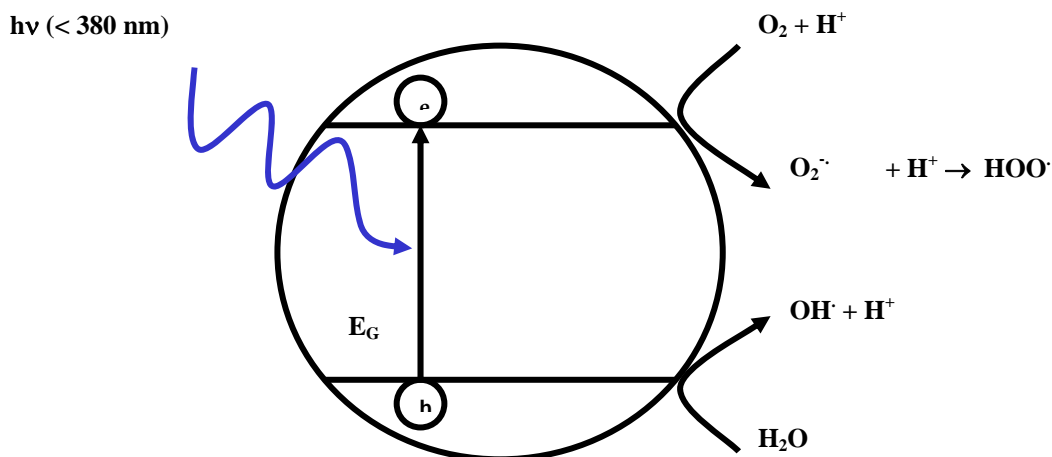
Due to the high reactivity and short lifetime of hydroxyl radicals, their recombination with  $H\cdot$  radicals is a very probable process, if the two types of radicals are not separated by diffusion beforehand. Therefore, the formation of  $H_2O_2$  is just a rather improbable side-reaction. In addition to that, the produced  $H_2O_2$  strongly absorbs UV radiation below 280 nm, which results in the formation of an excited state that easily results in the cleavage of the O-O bond.

The excitation of  $H_2O_2$  by UV radiation thus results in the photodecomposition of  $H_2O_2$  according to the following reaction scheme [5]:



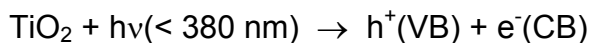
As a consequence, an efficient production of  $H_2O_2$  by the photochemical cleavage of  $H_2O$  is not feasible.

The application of a photocatalyst, such as  $TiO_2$  (anatase), completely changes the situation. It was proven that the formation of  $H_2O_2$  is caused by the subsequent reduction of oxygen dissolved in water [6].

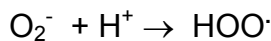


**Fig. 5:** Reaction scheme displaying the photochemical reactions of  $\text{H}_2\text{O}$  and  $\text{O}_2$  at an irradiated  $\text{TiO}_2$  particle surface.

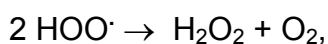
The first step in the reaction sequence is the formation of an electron-hole pair due to the absorption of a UV photon ( $< 380 \text{ nm}$ ).



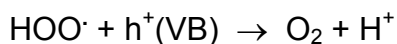
Subsequently, oxygen at the surface is reduced by the electron from the conduction band and the evolved peroxyradical is then protonated:



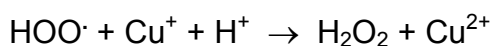
The produced hydroperoxyradical disproportionate according to



which thus results in the formation of  $\text{H}_2\text{O}_2$  and oxygen. However, a competitive reaction is the re-oxidation of the hydroperoxyradical at the  $\text{TiO}_2$  surface by reacting with a hole from the valence band:



To accelerate the conversion of hydroperoxyradicals into  $\text{H}_2\text{O}_2$ , the application of  $\text{Cu}^+$  was found to be an effective measure. The  $\text{H}_2\text{O}_2$  yield could be enhanced by a factor of 20 [4].



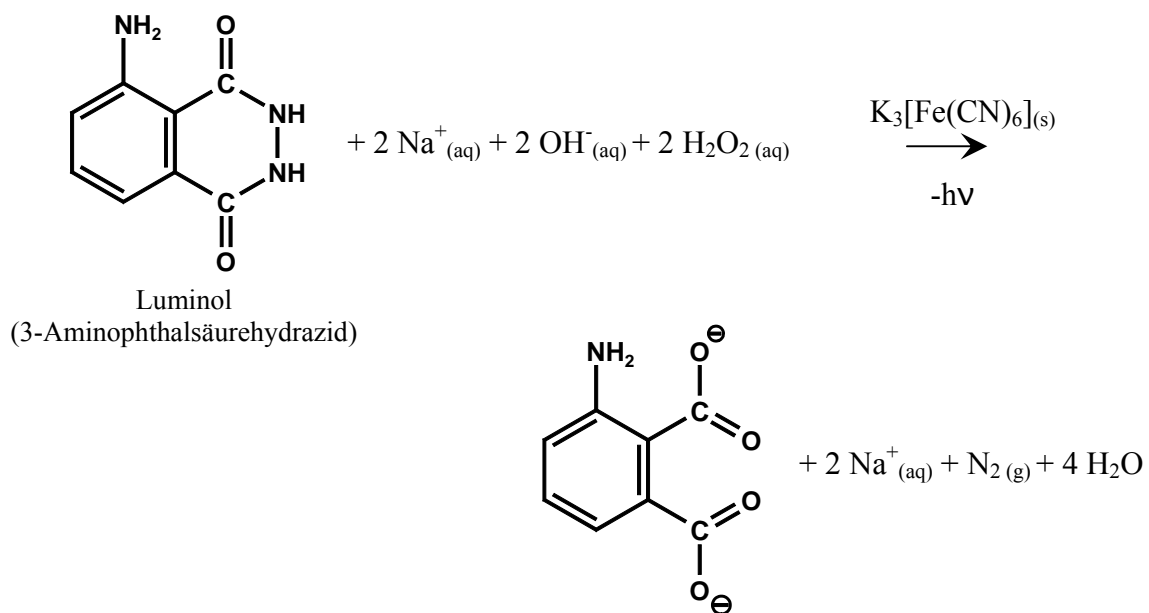
Afterwards, the  $\text{Cu}^{2+}$  is reduced at the surface of the  $\text{TiO}_2$  photocatalyst by taking up an electron from the conduction band.



To the author's opinion it is likely that not only  $\text{Cu}^{2+}$  can act as a redox catalyst to enhance the  $\text{H}_2\text{O}_2$  formation, but also other transition metal ions, from which coordination compounds with a similar oxidation/reduction potential as that of the  $\text{Cu}^{+2+}$  couple in aqueous solution exist. Transition metal ions of interest are thus  $\text{V}^{3+/4+}$ ,  $\text{Mn}^{2+/3+}$ ,  $\text{Fe}^{2+/3+}$ ,  $\text{Co}^{2+/3+}$ ,  $\text{Ni}^{2+/3+}$ , and  $\text{Ru}^{2+/3+}$ .

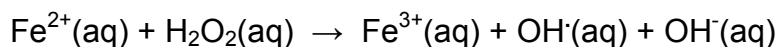
#### 4. Qualitative Detection of $\text{H}_2\text{O}_2$

A highly specific reaction is the oxidation of luminol in the presence of a catalyst, e.g.  $\text{K}_3[\text{Fe}(\text{CN})_6]$  or other  $\text{Fe}^{2+/3+}$ -containing species.



**Fig. 6:** Reaction scheme for the qualitative determination of  $\text{H}_2\text{O}_2$  by luminol.

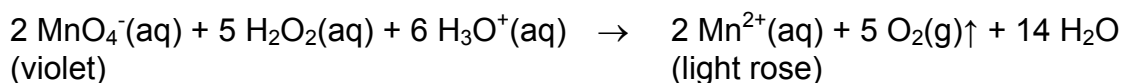
This reaction yielding in blue chemoluminescence is extremely sensitive and even applied for the forensic trace analysis of blood, which catalyses the decomposition of  $\text{H}_2\text{O}_2$  by  $\text{Fe}^{2+}$  present as the oxygen transport carrier in the hem ring.



This reaction is also known as the Fenton reaction.

#### 5. Quantitative Determination of $\text{H}_2\text{O}_2$

The standard process for the quantitative determination of the  $\text{H}_2\text{O}_2$  concentration of an aqueous  $\text{H}_2\text{O}_2$  solution relies on a redox reaction according to the following equation:



The strong color change can be exploited for the volumetric determination of the concentration of  $\text{H}_2\text{O}_2$  solutions, e.g. by a titration with a 1 M  $\text{KMnO}_4$  solution, which is drop wisely added until the color of the  $\text{H}_2\text{O}_2$  solution remains violet. This point indicates the complete consumption of  $\text{H}_2\text{O}_2$  due to the reduction of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ . From the consumed volume of  $\text{KMnO}_4$  solution and its concentration, one can easily calculate the concentration of the  $\text{H}_2\text{O}_2$  solution.

## References

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- [6] R. Cai, Y. Kubota, A. Fujishima, *Journal of Catalysis* **219** (2003) 214
- [7] World Patent WO2002/027071, Degussa AG (2002)