Electrochemistry of hydrogen peroxide in alkaline and acidic media

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From the fuel cell perspective, hydrogen peroxide is first an undesired potential intermediate of the oxygen reduction reaction to water. Because of its high oxidation potential, it can be very destructive to the membrane. Large efforts were therefore taken to avoid it production as fa as possible and protect the membrane as good as possible. On the other hand side in some applications were air is not available hydrogen peroxide is considered as an alternative oxidant. Finally, the desire to avoid chemicals having a negative influence on the environment has yielded in an increasing importance of hydrogen peroxide as chemical commodity. Here electrochemical production is discussed, as an alternative for world scale anthrachinone plants were local need for hydrogen peroxide exists.

A hydrogen peroxide is slightly more acidic than water in a strong alkaline environment it will mainly exist as peroxyle anion OOH⁻. Therefore, the chemical but also the electrochemical behaviour of hydrogen peroxides differs in the alkaline from the acidic environment. In recent years, Fraunhofer ICT has been involved in research of all three aspects of electrochemical reactions involving hydrogen peroxide. In this presentation, basic findings on the difference in the reactions between the alkaline and acidic environment will be discussed. An example of such difference is the electrochemical behaviour of glassy carbon electrodes in acidic and alkaline electrolyte, which either were saturated with oxygen or contained 1 mM H₂O₂. In case of oxygen-saturated electrolytes, the activity for oxygen reduction is several orders of magnitude higher in the alkaline than the acidic environment and shows only a small hysteresis whereas in the acidic environment a strong hysteresis is oberseved (cf. fig. 1). Thereby, the oxygen peroxide as recognisable by large ring currents in the ORR active potential region. In the acidic environment, the behaviour is different showing high hydrogen peroxide provide production at low and high potentials but not in between (cf. fig. 2).



In electrolyte with hydrogen peroxide addition, the activity of the glassy carbon electrode was generally low. In the alkaline environment, a small activity for the hydrogen peroxide oxidation reaction was observed throughout the tested potential region. In the acidic environment, the disc current seems to be dominated by double layer charging cf. fig. 3.



Fig. 3 GC disc electrode currents in different electrolytes containing 1mM $\rm H_2O_2$ recorded at 1600 rpm and 25 $^\circ C$