

VOLTA VOLTA

Shared Innovation Program VoltaChem: Electrification of the Chemical Industry

Electrosynthesis of hydrogen peroxide

R.J.M. Bisselink, J. van Erkel, M. Zijlstra / roel.bisselink@tno.nl

TNO / Utrechtseweg 48 / 3704 HE Zeist / The Netherlands



Hydrogen peroxide (H_2O_2) is a strong oxidizer, considered environmentally friendly and used for bleaching, chemical synthesis, waste water treatment and disinfection in various industries. Decentralised H_2O_2 production via electrochemistry minimises shipment, handling and storage and avoids the use of hydrogen, solvents and complex processing for catalyst recycle in case of the anthraquinone autoxidation process. H_2O_2 electrosynthesis is usually performed in strong alkaline solutions [1] in which H_2O_2 is least stable [2]. Furthermore, high H_2O_2 concentrations can have a negative effect by H_2O_2 reduction to H_2O . Utilisation of electrodialysis principles (Figure 1) proved to be effective in removing H_2O_2 as HO_2^- from the catholyte [3], which is however limited by the stability of the anion exchange membrane (AEM) [4]. In addition, potential applications are limited due to salts and/or acids used in the centre compartment or require complex H_2O_2 purification methods.



Figure 2: Polarisation curves of GDE (3.1 cm^2) in 0.1 M KOH (black line) with pure O₂ supplied at the backside and Ir-MMO (3.0 cm^2) in 0.1 M H₂SO₄ (red line) at 1 mV/s and room temperature (~20°C).

of batch-recycle operation. H_2O_2 production in the catholyte and centre compartment and the cell voltage are in line with the mathematical model (Figure



Figure 4: H_2O_2 concentrations during electrolysis at 1 A using a 10 cm² plateand-frame electrochemical cell in a batch-recycle set-up with continuous removal of H_2O_2 , centre compartment filled with Nafion NR50 beads and initially demineralised water.

based solid polymer electrolyte (SPE) in the centre compartment are successful and enables continuous production of ~70 g/L H_2O_2 for almost 100 hours at 64% current efficiency. The H_2O_2 product contains only 0.05 mM K⁺ and 4 mM SO_4^{2-} probably caused by non-ideality of ion exchange membranes. Design of the SPE appears crucial as energy usages of 11 to 80 kWh/kg H_2O_2 are obtained with various SPE structures.

OBJECTIVE

The objective of our research is to achieve H_2O_2 production using stable anion exchange membranes, mathematical modeling of the process and subsequently the development of an electrolyser concept towards salt (and acid) free production of H_2O_2 .

---- RESULTS

A gas diffusion electrode (GDE) consisting of a mixture of PTFE, graphite and acetylene black is used as cathode and iridium MMO coated titanium as anode. A minimum energy usage of 2.7 and 3.2 kWh/kg H_2O_2 is derived from polarisation curves (Figure 2) at 0.5 and 3.0 kA/m², respectively. Ion exchange membranes with an assumed area resistance of 4 Ω ·cm² increases energy usage to an acceptable 3.0 and 5.2 kWh/kg H_2O_2 .

The electrode kinetics are fitted to the Butler-Volmer equation and combined with diffusional transport of oxygen (GDE).

The electrode kinetics, mass transport (ext. Nernst Planck equation) and equilibrium chemistry are combined in a non-steady state model enabling simulation 3). 100 g/L H_2O_2 is achieved at high current efficiency, ~85%, with no deterioration noticed of the AEM (Neosepta AHA). Obtained water transport numbers of 2.9 and 3.5 mol/F for CEM and AEM respectively indicates a max. concentration of 120 g/l H_2O_2 . The initial energy usage of 16 kWh/kg H_2O_2 (mainly caused by iR drop in the aqueous electrolytes) increased to 40 kWh/kg H_2O_2 due to dilution effects in the centre compartment and illustrates the necessity of salt or acid addition which is undesired from a cost and processing perspective. Initial trials with PFSA





--- CONCLUSION & OUTLOOK

1. A concentration of $100 \text{ g/L H}_2\text{O}_2$ is achieved experimentally while maintaining the structural and functional integrity of the membranes.

- 2. The developed mathematical model describes essential parameters of the electrochemical process satisfactory.
- 3. Incorporation of SPE between both ion exchange membranes enables direct H_2O_2 electrosynthesis with low salt and acid content.

Next steps in our research include attempts to reduce energy usage by minimisation of iR drop through SPE and cell design optimisation.



Figure 1: Schematic representation of the used principle for electrosynthesis of H₂O₂

Figure 3: H_2O_2 concentrations and cell voltage during electrolysis at 5 A using a 100 cm² plate-and-frame electrochemical cell equipped with Nafion 117 and Neosepta AHA membranes. 2 litres $0.1 \text{ M H}_2\text{SO}_4$, 2 litres 0.1 M KOH catholyte and 0.3 litres $0.1 \text{ M K}_2\text{SO}_4$ were circulated through the anolyte, catholyte and centre compartments, respectively. Pure oxygen was fed to the backside of the GDE. The solid lines were obtained using the mathematic model.

REFERENCES

[1] D. Pletcher, Watts New 4 (1999), 1-7.
[2] J.A. Navarro et al., Chem. Soc., Faraday Trans. I, 80 (1984), 249-253.
[3] C. Kuehn et al., US4357217 (1981).
[4] C. Kuehn et al., J. Electrochem. Soc., 130 (1983), 1117-1119.

JOIN VOLTACHEM'S COMMUNITY: WWW.VOLTACHEM.COM/COMMUNITY

VoltaChem is powered by

