Algemene gegevens	
PPS-nummer	**TKI-BBE-1803**
Titel	**Electrochemical Hydrogen Peroxide (EHP) production**
Roadmap	**Chemische conversie**
Uitvoerende kennisinstelling(en)	*Universiteit Twente*
Projectleider onderzoek (naam en emailadres)	**Bastian Mei, b.t.mei@utwente.nl**
Penvoerder PPS (namens private partij)	**Nouryon (former AkzoNobel Pulp and Performance Chemicals)**
Contactpersoon overheid (indien relevant)	**-**
Adres van de projectwebsite	**-**
Werkelijke startdatum	**01-10-2018**
Werkelijke einddatum	**30-09-2019**

Goedkeuring penvoerder / consortium De eindrapportage dient te worden besproken met de penvoerder/het consortium. TKI BBE neemt graag kennis van evt. opmerkingen over de rapportage.	
De penvoerder heeft namens het consortium de eindrapportage	x goedgekeurd ☐ niet goedgekeurd
Evt. opmerkingen over de eindrapportage:	

Consortium	
Zijn er wijzigingen geweest in het consortium/de project-partners? Zo ja, benoem deze	No

Inhoudelijke samenvatting van het project	
Probleemomschrijving	Hydrogen peroxide (H_2O_2, HP) is an environmentally friendly oxidant used in multiple applications,[1-3] including (but not limited to) pulp and paper bleaching or wastewater treatment. In industry, the anthraquinone (AO) process is dominantly used to produce HP. However, this process relies on harmful organic solvents and the need for centralized production. Thus, it is important to find green alternatives which allow for decentralized production. Electrochemical hydrogen peroxide production is a promising alternative to the AO process. Although selective oxygen reduction (at the cathode) has been studied widely, selective water oxidation (at the anode) received considerably less attention. Thus, in this project, the anodic production of hydrogen peroxide was investigated.
Doelen van het project	The goal of this project was the feasible implementation of green hydrogen peroxide production through (photo)electrochemical means. Roughly, two main goals were defined:

	1. Develop electrodes suitable for the anodic production of hydrogen peroxide. In literature, $BiVO_4$ was reported to be an efficient (photo)electrocatalyst for the production of HP.[4-6] Therefore, the research was originally aimed on the production of $Bi(X)O_4$ materials for hydrogen peroxide evolution with X being Mo, V W and their combinations. 2. Evaluate different reactor geometries, allowing for full evaluation of the electrochemical HP processes involved (*i.e.*, obtaining relevant current densities and reliable stability data).

Resultaten	
Beoogde resultaten uit het projectplan	The following work packages have been defined: 1. Develop electrodes capable of electrochemically producing HP 2. Develop a suitable reactor for anodic HP evolution and test as-obtained materials, and find a suitable method to analyze the amounts of HP formed 3. Provide a literature survey on the current status of electrochemical HP commercialization
Behaalde resultaten	The obtained results are as follows: 1. In the original plan, we highlighted that we would focus on bismuth (Bi)-based materials. However, it soon became apparent to us that bismuth vanadate ($BiVO_4$) is a very unstable material when used for the (photo)electrochemical production of hydrogen peroxide. In subsequent research, we decided to test the electrochemical properties of more well-known materials, namely titanium dioxide (TiO_2) and fluorine-doped tin oxide (FTO). From those materials, FTO was the most suited material for anodic HP production. In a two-compartment cell with 2.0 M $KHCO_3$, we found Faradaic efficiencies of 4 to 5 % (within an operating time of 15 to 60 minutes) at a fixed working electrode current of 7.08 mA/cm^2, corresponding to an electrode potential of *ca.* 2.9 V vs. RHE. At a higher fixed potential of 3.2 V vs. RHE (corresponding to a current of roughly 13 mA/cm^2), higher Faradaic efficiencies of 5.4 and 6.4 % have been found at reaction times of 60 and 15 minutes, respectively. Importantly, the FTO was stable during the electrochemical experiments. We found, in accordance with literature,[4, 6] that usage of a bicarbonate-containing electrolyte is essential for efficient HP production. Surprisingly, despite old reports describing the evolution of HP through the electrolysis of sulfuric acid,[3, 7-8] we did not observe any activity using this type of electrolyte. To summarize, we were able to produce anodic hydrogen peroxide and gathered reliable benchmark data that will/have be used in submitted proposals. Furthermore, it is important to notice that we will still pursue electrode development using the $Bi(X)O_4$ class of materials 1) to mitigate stability issues with $BiVO_4$ and 2) to increase process selectivity. 2. We have been able to obtain a two-compartment cell capable of electrochemically producing hydrogen peroxide (acting as a batch reactor). A schematic of the reactor has been added in appendix A (at the end of the document). Stability of hydrogen peroxide in contact with individual parts of the reactor was verified to ensure that Faradaic efficiency measurements are reliable. Furthermore, within the collaboration with industry we found a reliable method to quantify the amounts of hydrogen peroxide produce. The method is based on spectroscopic analysis after addition of titanium oxysulfate ($TiOSO_4$) in acid to the sample solution. Although in literature a titration method

	based on potassium permanganate ($KMnO_4$) is reported,[4] we found this method to be unreliable (due to the absorption spectra being instable over time and demonstrating unexpected features in their shape). 3. A literature survey is included within a techno-economic study, which we expect to publish soon. In this study, we modelled the techno-economics of a photoelectrochemical (PEC) plant capable of producing hydrogen with concomitant anodic hydrogen peroxide formation. In the study, we demonstrate that such a PEC plant would financially be very advantageous compared to a 'classic' PEC plant producing hydrogen and oxygen. In fact, in an ideal situation, the H_2/H_2O_2 PEC plant even financially outcompetes hydrogen formation by conventional steam methane reforming. The techno-economic analysis highlights the significance of anodic HP production or alternative valuable chemicals at the anode for the implementation of a green hydrogen economy (paired electrolysis approach). It is important to note that the developed model can be easily adapted to an electrochemical H2/H2O2 process and allows for integration of other reactants/high-value compounds of interest. Using the developed model in ongoing research will enhance the impact of our studies and allow bridging the gap between fundamental and applied research.
Geef een toelichting op eventuele wijzigingen t.o.v. het projectplan.	Compared to the original project proposal, the following changes have been performed: - Rather than Bi-based electrodes, most research has been performed using FTO. This has been decided due to the instable nature of bismuth vanadate during the experiments, whereas FTO was clearly a stable electrocatalyst capable of producing HP. Therefore, studies were continued on FTO. - The literature study has been performed by presenting it as a part of a larger study describing the techno-economics of anodic HP production while producing H_2 at the cathode. - Originally, cathodic hydrogen peroxide evolution was to be incorporated within the project as well. However, obtaining anodic hydrogen peroxide production already needed full attention time-wise. Therefore, we have set out a vacancy for a master student to work on cathodic hydrogen peroxide production. Regretfully, no suitable student has been found for this project yet. The vacancy is nevertheless still open and we are actively looking for interested candidates.

Wat heeft het project opgeleverd voor	
Betrokken kennis instellingen (wetenschappelijk, nieuwe technologie, samenwerking)	The project has demonstrated promising potential on anodic HP production both from a theoretical and an experimental point of view. Theoretically, we have demonstrated that solar hydrogen evolution with concomitant hydrogen peroxide formation is very advantageous from a techno-economic perspective. Experimentally, our research implies that anodic hydrogen peroxide production is possible. Although the Faradaic efficiencies and HP production rates from literature have not been reached yet, we are currently still in a process of finding increased values for these scientific quantities. Thus, this PPS has been very important in lying foundations for anodic HP production studies. Collaboration-wise: 1. We experienced a very pleasant collaboration with our industrial partner Nouryon. For future research,

	Nouryon has been so kind to provide us with an electrochemical flow reactor (Electro MP Cell), which we are currently setting up in our lab. 2. In collaboration with the TU Delft, $BiVO_4$ samples have been made. As stated in the above, these samples were regretfully not suitable for HP production. 3. The techno-economic studies have been performed with contributions from Utrecht University.
Betrokken bedrijven (toepassing van resultaten in de praktijk, en op welke termijn?)	As-obtained results demonstrate the feasibility of anodic HP production. Although the research is in its infancy, we believe we have made the first steps to allowing us to fully understand the requirements for anodic H2O2 formation. Based on the obtained data we will define new research targets that will enable industrial implementation of process. Setting up an electrochemical flow cell will enable us to take the next steps to industrial implementation. Even though far from commercial scale there are important practical and commercial values from this project as it shows both the complexity and the potential of this new field. The techno-economic evaluation provides important information for decision makers outside academia and the results point out that fundamental understanding and collaboration between academia and industry is crucial for success.
Maatschappij (sociaal, milieu, economie)	Our techno-economic studies predict that successful anodic HP production will be an important step towards a renewable hydrogen economy. Substitution of oxygen with a valuable product (*i.e.*, hydrogen peroxide) seems to be a crucial step for the implementation of the industrial production of hydrogen through (photo)electrochemical means.
Evt. andere stakeholders (spin offs)	N/A

Follow-up	
Is er sprake van een of meer octrooi-aanvragen (first filings) vanuit deze PPS?	No
Komen er vervolg projecten? Zo ja, geef een toelichting (bv. contractonderzoek dat voortkomt uit dit project, aanvullende subsidies die zijn verkregen, nieuwe PPS)	Yes. This project has resulted in promising leads on anodic hydrogen peroxide production. However, the research is in its infancy and more work will be required before scientific breakthroughs worthy of publication can be made. A new PPS has been granted by TKI Chemie under the name CHEMIE.PGT.2019.007. Additional funds have been applied for within Marie Skłodowska-Curie Actions (EU funding)

Opgeleverde producten gedurende de gehele looptijd van de PPS (geef de titels en/of omschrijvingen van de producten / deliverables of een link naar de producten op de projectwebsite of andere openbare websites)
<u>Wetenschappelijke artikelen:</u> Although no scientific publications concerning anodic HP evaluation have been published within the time frame of the project, the techno-economics studies as a manuscript to Sustainable Energy & Fuels will be submitted shortly. Furthermore, we are planning to disseminate the method developed for reliable H2O2 production

Externe rapporten:
None

Artikelen in vakbladen:
None

Inleidingen/posters tijdens workshops, congressen en symposia:
Within the time frame of the project:
- Poster at the MESA+ day 2019 (Enschede, The Netherlands) entitled '*H_2O_2 as an attractive substitute for O_2 in electrochemical water splitting*' on 30 September 2019

Outside the time frame of the project, has occurred:
- Presentation at NanoGe 2019 (Berlin, Germany) entitled '*Towards anodic production of H_2O_2 as a financial attractive alternative to O_2 evolution*' on 5 November 2019

Outside the time frame, the next oral presentation has been approved:
- Presentation at N3C 2020 (Noordwijkerhout, The Netherlands) entitled '*Towards selective partial water oxidation to form hydrogen peroxide as a financially attractive substitute for oxygen in PEC water splitting*' on 4 March 2020

Outside the time frame, an abstract has been submitted for an oral presentation:
- Presentation at ESEE 2020 (Leeuwarden, The Netherlands) entitled '*Towards anodic H_2O_2 production as a profitable commodity chemical in PEC water splitting*' in June 2020

TV/ Radio / Social Media / Krant:
None

Overig (Technieken, apparaten, methodes etc.):
We have successfully obtained a batch reactor suited for the electrochemical production of H_2O_2.

References

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8. Ranganathan, S.; Sieber, V., Recent Advances in the Direct Synthesis of Hydrogen Peroxide Using Chemical Catalysis—A Review. *Catalysts* **2018,** *8* (9), 379.

Appendix A – Schematic of the batch reactor used for HP production.

① Anode (Area exposed ≈ 1.13 cm^2)

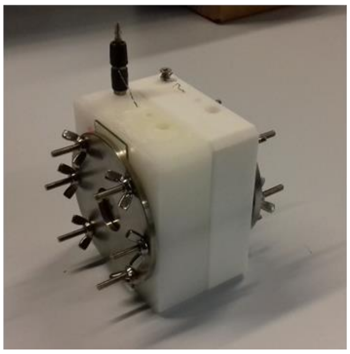
② Ag/AgCl reference electrode (3.0 M NaCl)

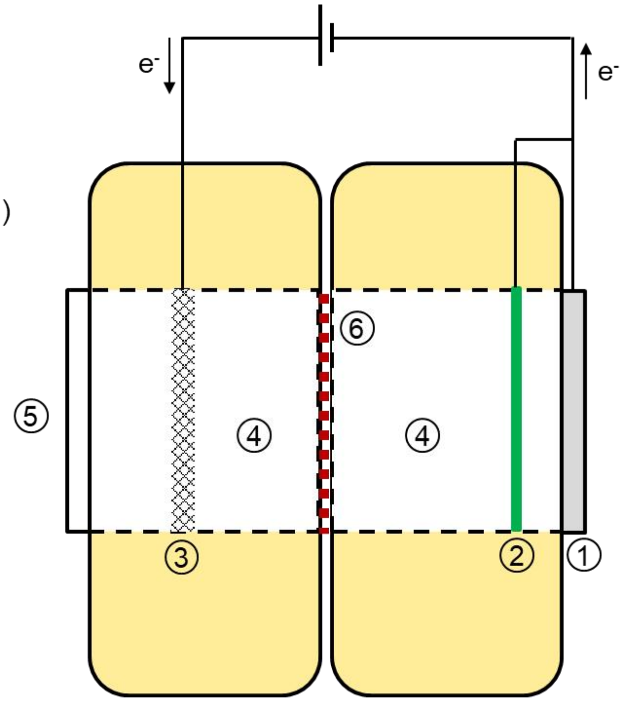
③ Platinum mesh cathode

④ Electrolyte 2 x (8.5 mL 2.0 M $KHCO_3$, pH ≈ 8.1)

⑤ Glass plate

⑥ Ion-diffusion membrane (bipolar membrane, FumaSEP)





Top left and right: schematic of the electrochemical cell used for HP production.
Bottom left: photograph of the electrochemical cell.