Factsheet **Project 1136**

Hydrogen economy based Advanced Oxidation Process

Water Research AUSTRALIA

Background

Excess electrical energy generated by renewable sources including photovoltaic systems during daylight hours could be used to power electrochemical water splitting to produce hydrogen (H_2) and hydrogen peroxide (H_2O_2), both of which are essential chemicals for the emerging hydrogen economy as fuels, feedstocks in chemical synthesis, or oxidizing agents in advanced oxidation processes. Water splitting traditionally uses freshwater, which is already a scarce resource in many countries including Australia. Additional consumption of freshwater for this purpose will increase operational costs of production and place additional stresses on water resources. In major Australian urban areas, large volumes of recycled wastewater (RWW) are generated by centralised municipal wastewater treatment plants (WWTPs), which could provide a valuable alternative water sources for future electrolysis. A potential disadvantage emerges when considering the potentially undesirable side effects of residual contaminants within RWW, which may reduce H_2 and H_2O_2 production efficiencies and reduce electrolyser lifespan. The required water quality for this process is thereby informed by the key impurities that impede electrochemical H_2/H_2O_2 production using RWW, establishing guidelines for electrolyser design and WWTP operations and improvements.

Key points:

- Solar-powered electrocatalytic H_2/H_2O_2 production using recycled water can help to alleviate stresses on freshwater resources.
- Recycled wastewater contains key impurities which affect electrochemical processes and electrocatalyst lifespan.
- Existing gaps include a comprehensive review of the required quality of recycled wastewater for H_2/H_2O_2 production by considering contaminants such as metal ions and organic compounds which persist after treatment processes.
- Addressing these gaps is necessary for the development of guidelines for electrolyser design and required wastewater treatment plant.

Principles of electrochemical water splitting

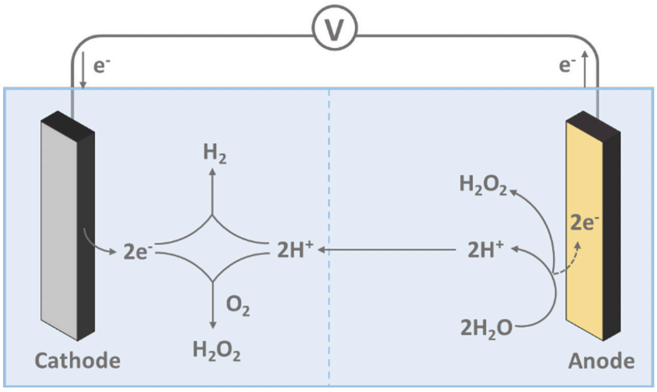

Figure 1. Schematic of the electrochemical water splitting process for H_2/H_2O_2 generation.

Hydrogen is an attractive energy carrier due to its high energy density and lack of polluting by-products. Hydrogen produced via water splitting (Equation 1) can be stored, transported, then oxidised as an energy source to achieve a carbon-neutral cycle. Another attractive product of water splitting is hydrogen peroxide (Equation 2 and 3) which can be utilised as a sustainable oxidation reagent within advanced oxidation processes or as an energy source for fuel cells. By connecting the electrodes with a renewable power source in series, H_2 is produced by hydrogen reduction at the cathode (HER, Equation 1), while H_2O_2 is simultaneously generated either from oxygen reduction reactions (ORR, Equation 2) at the cathode or water oxidation reactions (WOR, Equation 3) at the anode [1]. In acidic proton exchange membrane electrolysers (Figure 1), the generated protons at the anode are transported through a proton exchange membrane (PEM) to satisfy the electrochemical half reactions at the cathode. To drive H_2/H_2O_2 evolution, a minimum theoretical voltage for electrochemical water splitting is required to "straddle" the energy levels of hydrogen reduction and water oxidation [2]. In practical electrochemical processes, an additional bias voltage (overpotential) is also needed to drive the charge transfer process at the electrode/electrolyte interfaces, which reduces efficiency and increases energy consumption. Recent efforts have attempted to address this through extensive studies of low-cost electrocatalysts for efficient energy carrier production [3, 4]. For PEM water electrolysis, enhancing the stability of electrodes and proton exchange membranes is also critical to implementing the process for long-term and large-scale uses.[5]

$$2H^+ + 2e^- \rightarrow H_2\ (E_0 = 0\ \text{V}\ \textit{vs.}\ \text{RHE}) \qquad \text{(HER, Equation 1)}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2\ (E_0 = +0.68\ \text{V}\ \textit{vs.}\ \text{RHE}) \qquad \text{(ORR, Equation 2)}$$

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+\ (E0 = +1.77\ \text{V}\ \textit{vs.}\ \text{RHE}) \qquad \text{(WOR, Equation 3)}$$

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Impacts of electrolytes

Electrolytes pose impacts on reaction kinetics and electrode stability by participating in electrochemical redox processes and influencing mass transfer rates [6]. While conventional electrolysers work best within a high or low pH range (pH 13-14 or 0-1 respectively) at which sufficient concentrations of charge carriers can facilitate energy conversion reactions, there remains a mismatch between optimal conditions for HER (pH < 7) and WOR (pH > 7) [7]. A vast majority of electrocatalysts also tend to degrade at extreme pH values, which places constrains on the long-term reliability of electrolysers. Near-neutral pH values could avoid the potential degradation issues introduced by caustic electrolytes, so along with efforts to develop corrosion resistant materials electrocatalysts with wider pH operating ranges are being investigated.

In addition to the influences of pH, soluble ions and molecules in electrolytes have been reported to have significant impacts on the efficiency of electrochemical reactions. The electrocatalyst layers of electrolysers have a porous structure. HER, ORR and WOR reactions can only occur at the spatially confined sites around the interfaces between the catalyst layers and the proton membrane, called triple phase boundaries (TPB), where ionomers, reactants and electrically connected catalysts contact. The reaction rates of electrochemical reactions highly depend on the properties of TPBs and the proton transport ability of PEMs. Previous studies have already shown that electrocatalysts and membranes in electrolysers are susceptible to feed water impurities, particularly cations including Na^+, Ca^{2+}, Cu^{2+} and Fe^{3+} [8, 9]. While the mechanism of the metallic cation poisoning has not yet been fully understood, it is generally believed that these cations can occupy ion exchange sites in proton membranes and the ionomers in catalyst layers, reducing the proton mobility and increasing the over potential at cathodes and anodes. The active sites of electrocatalysts can also be blocked by organics and other impurities due deposits within interconnected catalyst layer pores, decreasing the intrinsic reactivity of the electrocatalysts. Further efforts will be required to identify which concentrations of feed water impurities are tolerable in long-term operation electrolyser operations.

Quality of recycled water

Table 1. Classes of recycled water and corresponding standards for biological treatment and pathogen reduction [11].

Water quality parameter	Unit	Class A	Class B	Class C
Turbidity	NTU	< 2	-	-
pH	-	6-9[5]	6-9[5]	6-9[5]
Biochemical oxygen demand (BOD)	mg/L	10	20	20
Suspended solids (SS)	mg/L	5	30	30
Residual chlorine	mg/L	1	-	-
E. coli	org/100 mL	< 10 *E. coli*	100 *E. coli*	1000 *E. coli*

Use of RWW from WWTPs presents as a potential solution to the high volumes of water required for electrochemical H_2/H_2O_2 evolution. In the Australian Guideline for Water Recycling, recycled water is defined as water that has been treated to fit-for-purpose standards for specific applications [10]. The Environment Protection Authority, Victoria provides threshold values of physical-chemical water quality (for example, turbidity and BOD) and *E. coli* limits for biological treatment and pathogen reduction (Table 1) [11]. While the majority of pollutants in wastewater are effectively removed in the current wastewater treatment processes, small amounts of contaminants (e.g. metal ions, organic components, nutrients, etc.) remain in RWW [10]. This wide range of potential impurities introduces a need to assess the feasibility of RWW as an electrolytic medium, which first requires the identification of key impurities in recycled water and the threshold concentrations at which interferences in electrolytic processes can be anticipated.

Summary

Electrolytic systems powered by renewable energy for the production of H_2 and H_2O_2 may assist the development of sustainable water treatment processes and efficient utilisation of excess energy. Beyond studies into active and robust electrocatalysts, the operation of electrochemical water splitting using RWW would provide an additional breakthrough for the translation of this technology into practical application. The identification of key impurities in RWW and an assessment on their impacts on electrochemical processes are necessary to assess the feasibility of utilising recycled water for electrochemical water splitting. Correlating the types and concentrations of key contaminants in recycled water with threshold values for effective electrolysis will inform guidelines on electrolyser designs and operation, which will indicate how existing WWTPs can be upgraded to facilitate energy efficient utilisation of H_2O_2 in advanced oxidation processes for water treatment.

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