



High-pressure water electrolysis: Electrochemical mitigation of product gas crossover



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ABSTRACT

Hydrogen produced by water electrolysis can be used as an energy carrier storing electricity generated from renewables. During water electrolysis hydrogen can be evolved under pressure at isothermal conditions, enabling highly efficient compression. However, the permeation of hydrogen through the electrolyte increases with operating pressure and leads to efficiency loss and safety hazards. In this study, we report on an innovative concept, where the hydrogen crossover is electrochemically mitigated by an additional electrode between the anode and the cathode of the electrolysis cell. Experimentally, the technique was applied to a proton exchange membrane water electrolyzer operated at a hydrogen pressure that was fifty times larger than the oxygen pressure. Therewith, the hydrogen crossover was reduced and the current efficiency during partial load operation was increased. The concept is also discussed for water electrolysis that is operated at balanced pressures, where the crossover of hydrogen and oxygen is mitigated using two additional electrodes.

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1. Introduction

At the beginning of the 19th century, it was discovered that water can be electrochemically decomposed by applying a voltage to two electrodes immersed in an aqueous solution. Hydrogen evolves at the cathode (-) and oxygen at the anode (+). Today, about 200 years later, water electrolysis is a promising solution for storing overcapacities of intermittent electric energy from renewables by means of chemical energy [1–5]. The hydrogen produced by electrolysis can be used for instance for methanation of CO₂ [6,7], combustion processes [8], and conversion back into electricity by fuel cells [9,10]. In order to provide emission-free transportation with green hydrogen, fuel cells are a promising technology for automotive applications [11]. Hydrogen pressures of about 600 bar are necessary to supply high volumetric energy densities for automotive applications [12,13]. The hydrogen produced by water electrolysis can be evolved under pressure in order to compress the gas [14–17].

Similar to the very first setups in the 19th century, the most simple approach for water electrolysis is the use of liquid electrolytes, where protons or hydroxide ions provide the conductivity of the electrolyte [2]. While nickel is an effective electrocatalyst in alkaline media [19–26], only catalysts based on the rare and expensive

platinum group have shown long-term durability and reasonable performance in acid media [1,25]. Liquid electrolytes require balanced pressures at the anode and cathode [16,27,28], which means that hydrogen compression during electrolysis also necessitates oxygen compression. Alternatively, solid polymer electrolytes (SPEs) coated with electrodes made of a mixture of the polymer and the catalyst can be used for water electrolysis [1,29,30]. These proton or anion exchange membranes (PEMs/AEMs) are basically solid acids or bases [31–39] that conduct protons or hydroxide ions in an aqueous phase. Fixed ions of opposing charge balance the charge of the conductive ions. Compared to liquid alkaline electrolytes, water electrolysis with SPEs is more efficient over a broader dynamic load range [40,1,19,30,28]. Due to the mechanical resistance of SPEs and their ability to withstand larger cathodic than anodic pressures [5,15], oxygen pressurization is no longer necessary [18,41]. However, owing to the acidity of PEMs [42], precious metals are employed as the catalysts. By using AEMs, both advantages of high performance and low cost catalysts may be combined. Unfortunately, AEMs have not shown long-term durability by now [43–47].

Thermodynamically, the energy required to compress a gas increases with temperature. Thus, the isothermal compression conditions during low-temperature water electrolysis are favorable compared to the isotropic or the adiabatic behavior of mechanical compression, where the temperature of the gas during the compression process increases [18,41]. Additional subsequent mechanical compression and the correlated maintenance issues

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and investment cost can be avoided by the direct hydrogen pressurization during its production employing water electrolysis. However, the hydrogen produced at the cathode and the oxygen produced at the anode can permeate through liquid or polymer electrolytes [48], a phenomenon commonly referred to as gas crossover [18,41,49]. Gas crossover increases with operating pressures and can cause safety issues due to explosive mixtures of hydrogen and oxygen [50,51,14]. Especially in the partial load range at low gas production rates, the influence of gas crossover on the anodic gas composition is problematic in terms of safety issues [18]. To reduce gas impurities, hydrogen and oxygen can be catalytically reacted to form water on the surface of a catalyst, for instance platinum. The catalyst can be immersed in the electrolyte, at the electrodes, or at the gas outlet [14,51]. The catalytic combustion of both gases solves safety issues by preventing both gases mixing. However, both hydrogen and oxygen permeation through the membrane cause a direct loss of the hydrogen produced and consequently reduce the efficiency of the electrolyzer [18].

At hydrogen pressures that are much larger than the oxygen pressures during SPE water electrolysis, the permeation of oxygen through the membrane is negligible compared to that of hydrogen [18]. In order to reduce the current efficiency loss and to improve the safety aspects, this study proposes an innovative electrochemical technique to reduce hydrogen crossover, which involves an additional electrode embedded in the electrolyte. Thereby, the way towards high-pressure electrolysis is paved. In the novel setup, the hydrogen permeating through the electrolyte is electrochemically oxidized at the additional electrode. An applied voltage between the additional electrode and the cathode electrochemically sends hydrogen permeating through the membrane back to the cathode. Hence, the current efficiency loss caused by hydrogen crossover can be reduced. Alternatively, the additional electrode can also be connected by a resistance to the anode. In this case, the hydrogen at the additional electrode electrochemically reacts with the anodic oxygen to form water, reducing the anodic potential caused by opposing overvoltages of the oxygen evolution and the oxygen reduction reactions.

2. Experimental

The common setup of a PEM water electrolyzer is discussed in the literature [1]. All measurements presented were conducted with a self made electrolysis cell with an active area of 25 cm² at a cell temperature of 85 °C. This cell consisted of titanium flow fields, which were plated with platinum at the anode and gold at the cathode. A sintered titanium body (GKN) with a thickness of 1.3 mm and grain sizes of 100 μm was used as anodic current collector, while three carbon papers (Toray, TPG-H-120) were employed as cathodic current collector. A PTFE gasket sealed the anode and a silicone gasket was used for the cathode sealing. Individual water circulation loops fed the anode and the cathode with water, respectively.

Nafion® (DuPont) membranes were used as PEMs. They were coated with self made catalyst layers by decal transfer [52,53]. The catalysts inks were applied by a squeegee on a PTFE foil, as discussed in the literature [52,53]. Iridium oxide (Johnson Matthey) with a loading of 2.2 mg/cm² and a Nafion® content of 25% was used as the anodic catalyst layer, while the platinum-based catalyst HiSpec9100 (Johnson Matthey) with 0.8 mg/cm² and a Nafion® content of 20% was used for all other catalyst layers. The catalyst layers were hot-pressed at 145 °C on Nafion® N1135 membranes. One membrane was coated with two platinum-based catalyst layers on each side. Another membrane was coated with a platinum catalyst layer on one side and an iridium oxide catalyst layer on the other. The two N1135 membranes were layered on top of each other, so that the iridium oxide catalyst layer face

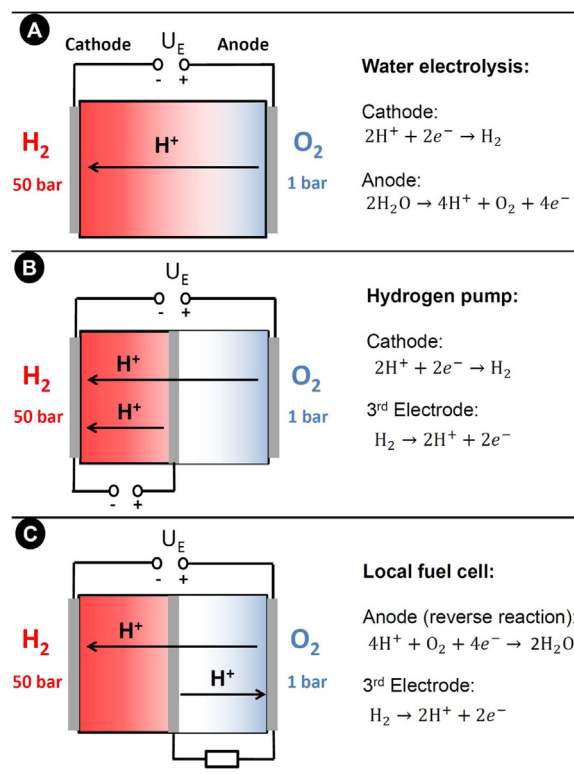


Fig. 1. Left: Setups for the electrochemical mitigation of hydrogen cross-permeation through the membrane during differential pressure water electrolysis. The red and blue shadings represent the concentrations of hydrogen and oxygen in the electrolyte. Hydrogen is permeating from the cathode to the anode (from left to right), while oxygen is permeating in the opposite direction starting from the anode. Right: Electrochemical reactions at the electrodes of the different setups. (A): Acid water electrolysis. The reactions at the anode and the cathode also occur for the other setups. (B): Connection of the additional electrode to the cathode by a power supply. The hydrogen that permeates from the cathode to the additional electrode is electrochemically sent back to the cathode. (C) Connection of the additional electrode to the anode by a resistance. The hydrogen at the additional electrode electrochemically reacts with anodic oxygen, reducing the anodic overpotential.

upwards. Between the membranes an expanded titanium mesh of 50 μm thickness (Dexmet) was immersed, which served as an electrical contact for the catalyst layers between the membranes. By hot-pressing at 145 °C, both membranes and the titanium mesh were melted together. The titanium mesh was greater than the membrane electrode assembly. The uncovered part of this mesh was electrically contacted by crocodile clips. Therewith, the additional electrode between the anode and cathode was realized.

All measurements were conducted under controlled current (galvanostatic). To supply the current for the electrolysis reaction, a Sorensen XTR 6-110 power supply was used. For the hydrogen pump configuration in Fig. 1B, a Biologic HCP-1005 potentiostat was used to connect the additional electrode with the cathode. In order to connect the additional electrode to the anode (Fig. 1C), a current controlled electric load (Höckerl and Hackl GmbH, ZS Electronic Load) was used. The anodic hydrogen content was measured using a K1550 gas analyzer (HITECH Instruments) as described in our former study [18]. The absolute error of the measurement of the percental hydrogen content at the anode was approximately ±0.15 %.

3. Results and discussion

In the following, the ability to mitigate the hydrogen crossover during PEM water electrolysis by an additional electrode according

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