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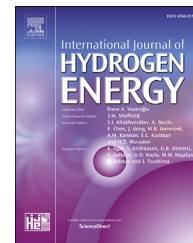
Improved operation of SO$_2$ depolarized electrolyser stack for H$_2$ production at ambient conditions

CrossMark

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ABSTRACT

In this paper, the performance of a robust SO$_2$ depolarized electrolyser (SDE) stack that involves neither Pt catalyst nor carbon compounds at ambient conditions is demonstrated. In particular, the effect of different anolyte flow configurations to the overall H$_2$ production rate and SO$_2$ carry-over phenomenon is presented. These results indicate that serpentine anolyte flow (U-configuration) provides higher SO$_2$ conversion, however, results in a more severe SO$_2$ carry-over phenomenon due to increased membrane-electrolyte interface. In addition, individual unit cells in the stacks are monitored for further understanding about the different operational environment in each cell and to provide guidelines for future SDE stack design.

Introduction

In order to fulfil CO$_2$ emission reduction for the prevention of the climate change cost efficient replacements for fossil fuels are needed. The traffic sector is responsible for 1/3 of the total CO$_2$ emissions [1], however, for hydrocarbon fuels in transportation applications few alternatives are available. Electric vehicles with Li ion batteries will initiate the change, thus to entirely replace hydrocarbon fuels also other technologies need to be develop. One of the most promising alternatives is hydrogen that can ensure the long operation distance as well as fast refuelling required in some applications [2]. Hydrogen vehicles produce no CO$_2$ emissions during operation, thus also hydrogen production must fulfil the same criteria. A traditional considered technique is water electrolysis powered by renewable sources where the water splitting reaction occurs at the anode

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23 \, V \quad (1)$$
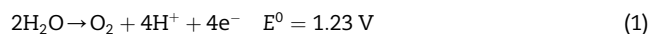
and the hydrogen production at cathode.

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0 \, V \quad (2)$$

Nevertheless, the water electrolysis requires high over voltages (the theoretical is 1.23 V vs. practical 1.7—2.2 V) leading to high electricity demand and therefore higher hydrogen cost. Additionally, high operation voltage at the anode requires unique, high cost materials further increasing the hydrogen cost. An alternative process — sulphur dioxide depolarized electrolysis (SDE) — has been developed where SO$_2$ is purged to the anode electrolyte and is electrochemically oxidized to sulfuric acid and hydrogen:
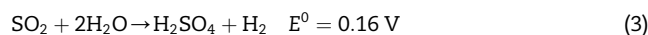
$$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2 \quad E^0 = 0.16 \, V \quad (3)$$

Such overall reaction occurs at significantly reduced over voltage [3], thus requiring less electrical energy and facilitating the integration of renewable energy to the process. In addition, the anode potential decreases widening the options for cell materials. If H_2 is the only desired product, SDE can be combined to hybrid sulphur cycle (HyS) process, the sulfuric acid produced can be cracked back to SO_2, H_2O and O_2 at high temperature step [4]. Alternatively, in co-production of H_2 and sulphuric acid industrial SO_2 gas emissions can be utilized as a reactant described by Outotec® Open Cycle process [5]. The SDE system proposed here is one possible configuration but also other approaches have been reported with liquid or gaseous SO_2 feed [6–9].

Common for all SDE systems is the cell structure that is similar to polymer electrolyte membrane (PEM) water electrolyser systems: two electrodes and a proton conductive polymer membrane as a separator material between the anode stream (anolyte) and cathode stream (catholyte) as presented in Fig. 1. The anolyte consisting of dissolved SO_2 in diluted H_2SO_4 solution is fed to the anode, where SO_2 oxidizes to sulphuric acid along producing protons and electrons according to reaction:

$$\text{Anode}: \quad SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^- \tag{4}$$
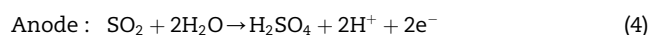
The PEM separator works as a proton conductor but repels electrons which are transported to the cathode via outer load where they meet the protons and form hydrogen gas:

$$\text{Cathode}: \quad 2H^+ + 2e^- \rightarrow H_2 \tag{5}$$

For economic operation and relevant H_2 production volume, the single cell configuration must be scaled up that can be performed either by increasing the cell geometric size or connecting the cells in series which increases the operating voltage of the stack. In Fig. 1 a SDE stack with 5 unit cells and their electrolyte flows are presented. Usually, when proceeded from a single cell experiments to stack level some of the issues encountered at the single cell level become negligible, however, new challenges are faced: such as higher carry-over rate, uneven current distribution on the bipolar plate surface that can create a hot spot accelerating degradation [10] or uneven electrolyte flow to different unit cells. In order to take this technology forward, stack experiments are vital to discover the limiting steps for high volume H_2 production.

To build stack bipolar plates introduced in PEM fuel cells and electrolysers are utilized: the anode reaction takes place on one side of the plate and the produced electrons are conducted through the plate to other side that acts as the cathode of the following unit cell (Fig. 1). For these bipolar plates various materials have been proposed however, the most used materials are carbon based that have optimal combination of thermal and electrical properties [11] or stainless steel based due to cost efficiency and plasticity [12,13]. Thus, electrolysers are stationary applications lowering the relevance of stack weight in comparison to PEM fuel cells and therefore in this study stainless steel plates were selected. Even stainless steel 316 has been utilized in SDE environment with good corrosion stability [7], but in particular, stainless steel 904L was selected due to high corrosion resistance in PEM fuel cell [14,15] and SDE environments [16].

Considering the main difference between PEM fuel cell, PEM water electrolyser and SDE is the nature of the electrolytes: in the first application both electrolytes are humid gases, in the second pure water while in the third the anolyte is SO_2 dissolved in sulphuric acid and the catholyte is sulphuric acid solution. In the first two cases no severe carry-over problem of reactants occurs thus, the crossover of the produced H_2 needs to be taken into consideration if pressurized H_2 gas is aimed [17]. This results a little interest for electrolyte flow control in the stack even though heterogeneous distribution of the reactants to different unit cells could decrease the lifetime of that unit cell as reported for PEM fuel cell stacks [18]. These gaseous electrolytes are fed to the stack as the Z
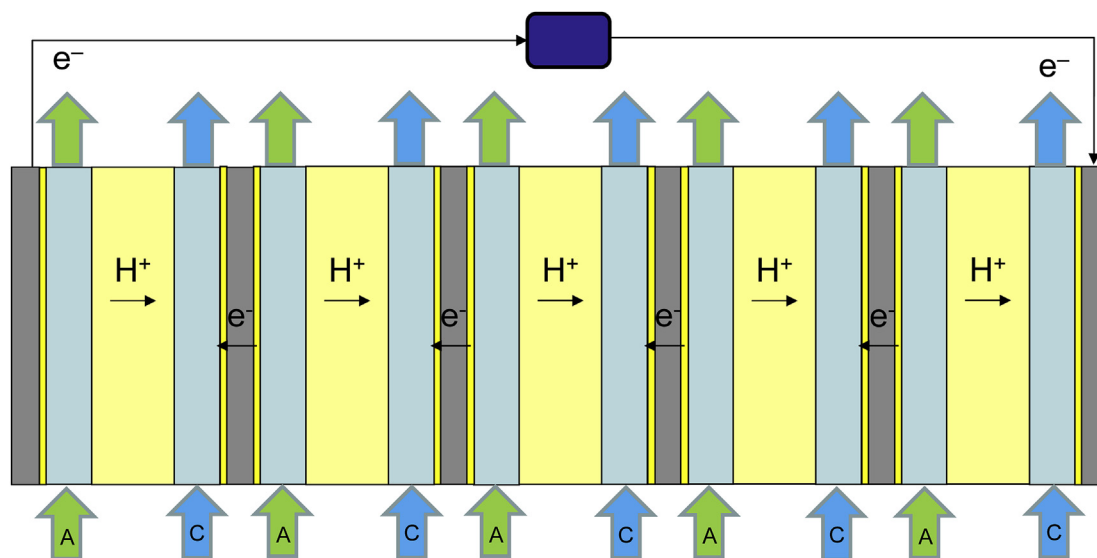
Fig. 1 – **PEM SDE module with 5 cells with the movement of the protons and electrons in the cell. Green arrows (A) indicate anolyte stream in Z-configuration stack and blue arrows (C) catholyte stream in both configurations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)**