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# Improved operation of SO<sub>2</sub> Depolarized Electrolyser Stack for H<sub>2</sub> production at ambient conditions

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## Abstract

In this paper, the performance of a SO<sub>2</sub> depolarized electrolyser (SDE) stack involving neither Pt catalyst nor carbon compounds at ambient conditions is demonstrated. In particular, the effect of different anolyte flow designs to the overall H<sub>2</sub> production rate and SO<sub>2</sub> carry over phenomenon is presented. Based on the results it can be concluded that serpentine anolyte flow (U-configuration) provides higher SO<sub>2</sub> conversion, however, simultaneously it results in a more severe SO<sub>2</sub> carry-over phenomenon. In addition, individual unit cells in the stacks are monitored for further understanding of the different operational environment in each cell in the stack and to provide guidelines for future SDE stack design.

*Keywords: Sulphur depolarised electrolyser, Stack, bipolar plates, hydrogen production*

## Highlights:

- Anolyte flow field optimization increased 40 % of the stack efficiency
- SO<sub>2</sub> carry-over is more severe in SDE stack in comparison to single cell
- Bipolar plate resistance does not influence strongly on cell performance

## 1 Introduction

In order to hinder climate change replacements for fossil fuels are needed. In 2004, the traffic caused around 1/3 of the total CO<sub>2</sub> emissions in the United States [1], however, few alternatives for hydrocarbon fuels are available for transportation applications. One of the most promising alternatives is hydrogen: it ensures the large distance transport that the customers claim for. Hydrogen

vehicles produce no CO<sub>2</sub> emissions during operation, thus, to obtain full carbon neutrality 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



And the hydrogen production at cathode

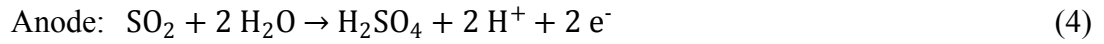


Nevertheless, the water electrolysis requires high over voltages to occur (the theoretical is 1.23 V vs. practical 1.7 - 2.2 V) leading to lower efficiency and higher hydrogen cost. An alternative process - sulphur dioxide depolarized electrolysis (SDE) - has been developed where SO<sub>2</sub> is added to the anode space and it is electrochemically oxidized to sulfuric acid and hydrogen:



Such overall reaction occurs at significantly reduced overvoltage [2], thus requiring less electrical energy and facilitating the integration of renewable energy to the process. In SDE process, sulfuric acid can be cracked back to SO<sub>2</sub> creating a cyclic process called hybrid sulphur cycle (HyS) [3]. Alternatively, industrial SO<sub>2</sub> gas emissions can be utilized as a reactant in co-production of H<sub>2</sub> and sulphuric acid known as the Outotec® Open Cycle [4]. For SDE structurally similar cell set up than for polymer electrolyte membrane (PEM) water electrolyser can be applied having 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 consists of dissolved SO<sub>2</sub>

in diluted  $\text{H}_2\text{SO}_4$  solution that is fed to the anode, where  $\text{SO}_2$  oxidizes to sulphuric acid producing proton and electrons according to reaction:



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:



Different SDE single cell configurations have been reported aiming for material and cell optimization [5-8].

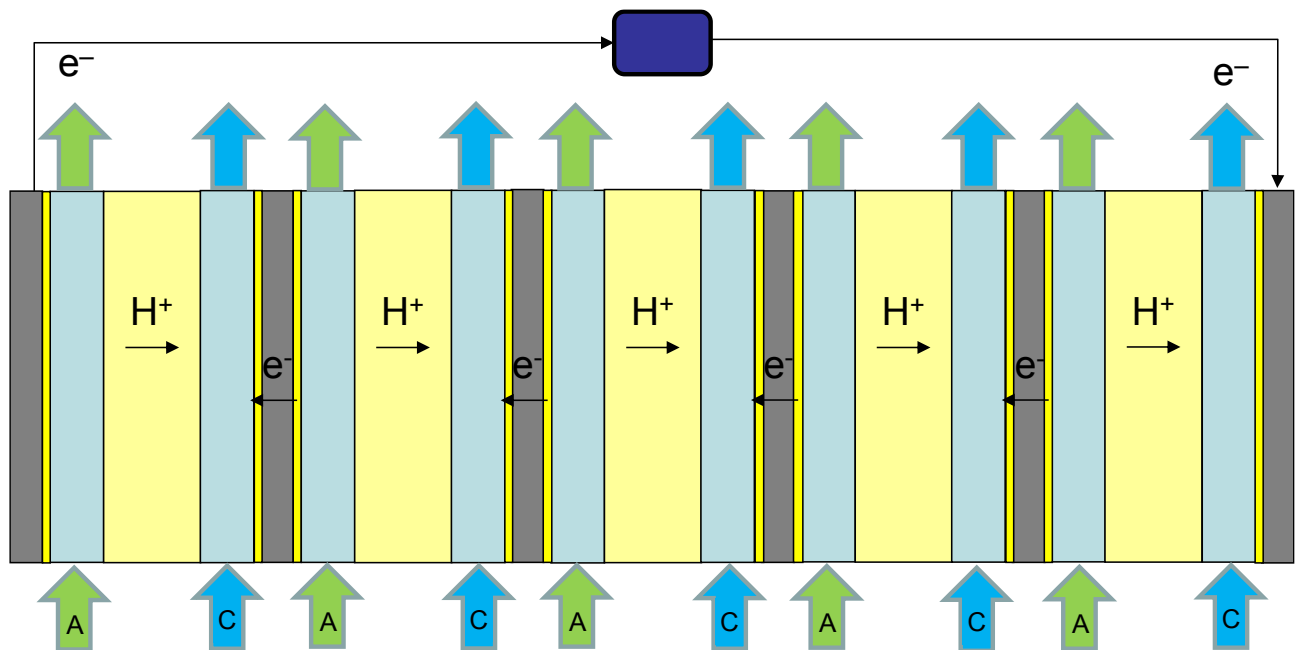


Fig. 1. PEM SDE module with 5 cells with the movement of the protons and electrons in the cell. Green arrows (A) indicate anolyte stream in Z-configuration stack and blue arrows (C) catholyte stream in both configurations.

For economic operation and relevant H<sub>2</sub> production, the single cell configuration must be scaled up to obtain. This may occur by both increasing the plate geometric size as well as connecting the cells

in series which increases the operating voltage and  $H_2$  production volume. In Fig. 1 a SDE stack with 5 unit cells and their electrolyte flow is shown. Usually, when proceeded from a single cell to stack some of the issues encountered at the single cell level become negligible, however, new challenges are faced. In order to take this technology forward, stack experiments are vital to discover the limiting steps for high volume production.

To build a stack bipolar plates known in PEM fuel cells and electrolyzers are utilized: at one side of the plate the anode reaction occurs and the produced electrons are conducted through the plate to other side that acts as the cathode of the following cell (Fig 1). For decades different material solutions for the bipolar plates have been studied. In PEM fuel cell conditions carbon materials are the most used due to its optimal combination of thermal and electrical properties [9]. In addition, stainless steel is also favorable since it is robust, easy to process and cost efficient [10,11]. Especially stainless steel 904 L has shown high corrosion resistance in PEM fuel cell and SDE environments [12,13].

Considering the electrolyte the main difference between PEM fuel cell, PEM water electrolyser and SDE is the form of the electrolyte: in the first application both electrolytes are gaseous, in the second pure water while in the third one the anolyte is  $SO_2$  dissolved in sulphuric acid and the catholyte is sulphuric acid solution. In the first two cases no severe cross-over problem of reactants occurs at ambient systems, however, the crossover of the produced  $H_2$  needs to be taken into consideration if pressurized  $H_2$  gas is aimed [14]. This results in 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 cell as reported for PEM fuel cell stacks [15]. Nevertheless, the main efforts in these applications are focused on the flow field optimization for individual unit cells [16,17]. In SDE, the flow configuration in stack design presents especial interest due to importance to separate the anode and cathode reactants: the separator membrane has pores for water transport allowing  $SO_2$  carry-over

through the membrane to the cathode where possible parasitic reactions may occur. The most common parasitic reactions are  $\text{SO}_2$  reduction to sulphur and  $\text{H}_2\text{S}$  [18]. For ensuring efficient SDE operation these side reactions should be avoided. In the stack design this issue becomes even more significant since the area of membrane-electrolyte interface is increased.

For PEM fuel cell stack, the gaseous electrolytes are fed as the Z configuration where the same flow is divided into each unit cells and collected at each outlet [19] that is also the case for Electrocell stack system (Z-configuration, Fig. 2). In this study, the catholyte flow remained as Z-configuration in all experiments to ensure efficient gas collection from the unit cells. However, two different anolyte flow options were tested: in Z-configuration the  $\text{SO}_2$  concentration in the anode compartment on each unit cell is identical and in U-configuration the same electrolyte enters each unit cell as a serpentine flow.

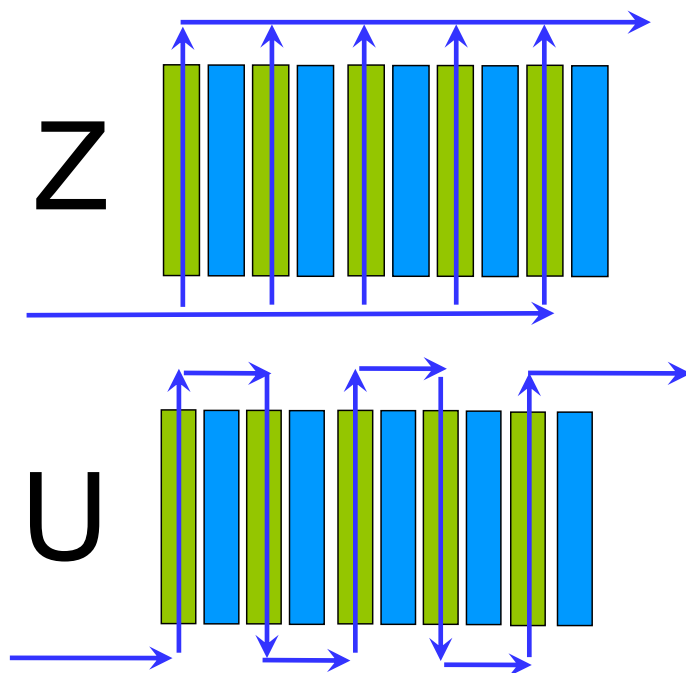


Figure 2. Different anolyte flows in the SDE stack: in Z-configuration the same anolyte will be directed to each cell, in U-configuration the output of the cell is input to the next unit cell and  $\text{SO}_2$  concentration decreases in each cell. Green blocks correlate to anolyte streams, blue catholyte streams (always Z-configuration).

Demonstration for SDE stacks has been presented previously for pressurized liquid electrolyte systems [20] and for ambient gas-phase systems [21]. However, these approaches have suffered some unexpected challenges. For pressurized systems it is very demanding to find suitable materials that can withstand the pressurized conditions: in case of large stacks it is not reasonable to have an individual fluid port for each cell [20]. As for the gas –phase system challenges with the bipolar plate corrosion was observed [21]. In these applications, carbon based materials are often used for catalyst support, gas diffusion layers or as composites in bipolar plates. Especially in SDE stacks, the control of individual cell potential can be demanding. If the potential in any of the cells increases rapidly due to a malfunctioning, carbon corrosion in any of the carbon components might occur already at quite low potential [22], thus, reducing the lifetime of these stacks.

The aim of this paper is to demonstrate the performance of a liquid fed SDE stack at ambient pressure. This stack set-up without Pt catalyst or carbon compounds offers a less demanding environment for all stack materials. Especially, an interest in exploring the effect of different anolyte configurations to the overall H<sub>2</sub> production rate and SO<sub>2</sub> carry-over phenomenon is explored. In this work two anolyte flow configuration are studied: the direct addition of the same electrolyte to each unit cell (Z-configuration) and the serpentine flow (U-configuration).

## **2 Experimental methods**

As a electrolyser stack, a commercial multi cell configuration from Electro MP Cell (ElectroCell) was used. The bipolar plates used were stainless steel plates (904L, Outotec) with 15 cm x 18,3 cm diameter and Au coated prepared with the proprietary low temperature arc-assisted PVD-method for both sides. The obtained layer thickness of the coating was  $1 \pm 0.2 \mu\text{m}$ . These bipolar plates worked as electrodes each having a surface area of 100 cm<sup>2</sup> and their characterization have been reported

elsewhere [5]. As a separator, commercial Nafion® 117 membrane (FuelCellsEtc.) was used and pre-treated by boiling firstly in 5 w% H<sub>2</sub>O<sub>2</sub> solution for 30 min and secondly in MQ water for 30 min. There was no need for ion exchange by boiling in H<sub>2</sub>SO<sub>4</sub> solution (as done in PEM fuel cell cases [23]) because in SDE the strong 15 w% H<sub>2</sub>SO<sub>4</sub> electrolyte ensures the ion exchange. The stack was assembled with 5 cells in series as follows: end plate, bipolar plate, cathode flow field, membrane, anode flow field, bipolar plate, each having an insulator gasket in between. A short video of assembly is available project web pages (<https://sol2hy2.eucoord.com/>). The stack was then tightened using 10 screws and with 12 Nm torch.

Electrolytes were 15 wt% H<sub>2</sub>SO<sub>4</sub> solutions (Merck, p.a) that were diluted the previous day allowing the concentration and temperature to settle. The 22 l of both electrolytes were fed to the system with pumps and the electrolyte flows were controlled to be 20 l h<sup>-1</sup> to the whole stack, and the estimated flow to each unit cell was 4 l h<sup>-1</sup>. From the stack, the electrolytes were circulated back to the storage tank and reused mimicking industrial process. SO<sub>2</sub> (AGA, 3.8) was added to the system by purging it to the anolyte tank with 1 bar pressure. The amount of fed SO<sub>2</sub> was followed by periodic titration (Titiline) of the anolyte with 0.5 M (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solutions (Sigma-Aldrich, p.a.) and electrochemically with polarization curves. Changes in the electrolyte acid concentration were monitored by titration with 2 M NaOH (Sigma-Aldrich, p.a.).

The electrochemical analysis was performed with IviumStat potentiostat equipped with a 40 A booster. When stabilizing, the cell was continuously monitored with open circuit voltage (OCV). To further characterize the cell polarisation curves from OCV to 8.5 V potential (corresponding around 1.7 V per cell) with 2 mV s<sup>-1</sup> sweep rate were conducted. In addition, electrochemical impedance spectroscopy (EIS) experiments were performed at 1.5 V for unit cells and at 7.5 V for the stack. These EIS experiments were made under potentiostatic control to avoid damage to the bipolar plates

in case of sudden voltage peaks, with a frequency range from 100 kHz to 0.1 Hz and with amplitude selection of the sinusoidal excitation signal of 10% of the studied potential. After constant SO<sub>2</sub> concentration in the anolyte was obtained and no change in the electrochemical behaviour in polarization curves was observed, electrolysis at constant 4 A current was performed. During the electrolysis the voltage of the stack and the unit cells were monitored with the potentiostat and with multimeter (Hewlett Packard 34420A Nano ), respectively. In addition, produced gas flow rates were detected with a flow meter (Brooks, T96987) and liquid samples of anolyte and catholyte were taken every 30 min for titration analysis. Another identical electrolysis was driven at 24 h of the SO<sub>2</sub> feed to study the effect of SO<sub>2</sub> carry-over on the SO<sub>2</sub> concentrations in both electrolytes and the potential of unit cells. After the experiment, the cell was taken apart and the bipolar plates analysed.

### 3 Results and discussion

As in industrial applications a constant hydrogen production rate was aimed and therefore both cells were operated at a constant current mode of 4 A. The cell was set up the day before the experiments with the acid electrolyte to stabilize overnight, however, the SO<sub>2</sub> was introduced only in the morning of the experiments. Firstly, the results of the whole cell are shown and after that the more detailed individual unit cell level results are described.

#### 3.1 *SDE stack overall performance*

The results of the whole stack are presented showing the changes in anolyte and catholyte SO<sub>2</sub> concentrations (Fig. 3), the hydrogen production profiles (Fig. 4) and the calculated current efficiency (Table 1) for each anolyte flow configuration. In the SO<sub>2</sub> concentration profile (Fig. 3) it can be seen that at the beginning of the experiment only acid electrolytes were in the cell after which the SO<sub>2</sub> feed was initiated. The first 1.5 h SO<sub>2</sub> was fed to the anolyte and the corresponding concentrations increase

steadily. After 1.5 h from the SO<sub>2</sub> feed the first electrolysis at 4 A current was run for 3.5 h (first yellow area in Fig. 3) and the second electrolysis was run on the following day from 24 h of the SO<sub>2</sub> feed initiation to observe the effect of SO<sub>2</sub> carry-over on the catholyte. In addition, the SO<sub>2</sub> appearance to the catholyte is shown in the right side of Fig. 3.

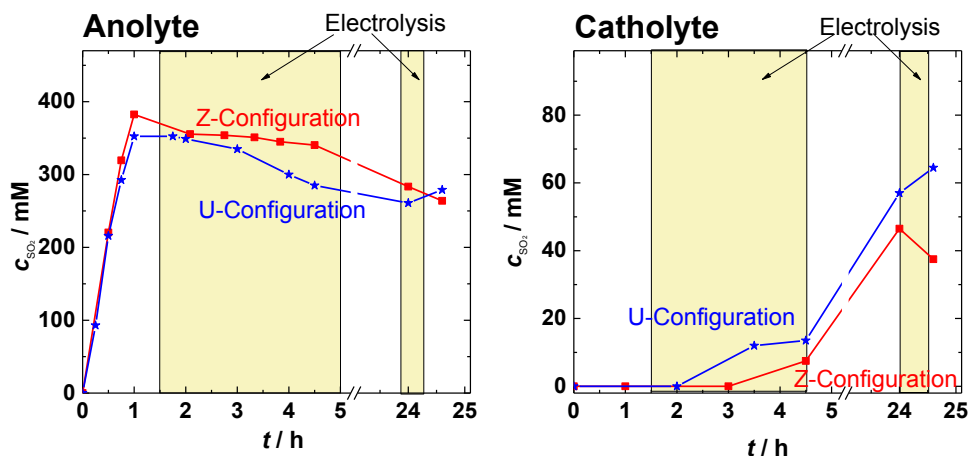


Fig. 3 The SO<sub>2</sub> concentration in the anolyte (left) and in the catholyte (right) for both flow configurations. The yellow areas indicate the electrolysis runs at day 1 and day 2.

The initial SO<sub>2</sub> concentrations were 380 mM and 360 mM for the Z- and U-configuration, respectively. According to our experiments the concentration of SO<sub>2</sub> is not limiting the stack performance as long as it stays above 200 mM. Because of the circulated electrolytes and large anolyte volume (22 l) the concentrations remain unchanged for the first hour of the electrolysis, after which in the Z-configuration only a small decrease in the SO<sub>2</sub> concentration is noticed due to fact that only part of the SO<sub>2</sub> is able to react in the cell. Contrary to Z-configuration in U-configuration the SO<sub>2</sub> concentration clearly reduces below 300 mM during the first electrolysis indicating that the SO<sub>2</sub> conversion in the cell is enhanced.

In catholyte there should not be any SO<sub>2</sub> present at all, however, due to SO<sub>2</sub> carry-over through the membrane [18] after few hours some SO<sub>2</sub> appeared at the catholyte (Fig. 5, right). As was expected, because of the 5 times larger membrane-electrolyte interface of the stack configuration a clear

indication of detected amount of  $\text{SO}_2$  can be observed already during the first electrolysis. However, in the case of the U-configuration the  $\text{SO}_2$  carry-over phenomenon is more prone. This could be due to the fact that the same electrolyte is in contact with the membrane surface 5 times (individually in 5 different cells) whereas in the Z-configuration the same electrolyte only passes through one cell. The increased  $\text{SO}_2$  amount of the catholyte in the U-configuration could also be partly due to more efficient proton transport through the membrane, increasing the overall flow from anode to cathode. For the second day electrolysis (24 h after the  $\text{SO}_2$  feed), it can be noted that the  $\text{SO}_2$  concentration has decreased in the anolyte and increased in the catholyte due to  $\text{SO}_2$  transport through the membrane. The values over night at the catholyte are around 5-6 times larger than at the end of the first electrolysis indicating that  $\text{SO}_2$  carry-over is significantly affected by the large anolyte-membrane interface in the stack clearly having an effect on the long term operation of the SDE stack.

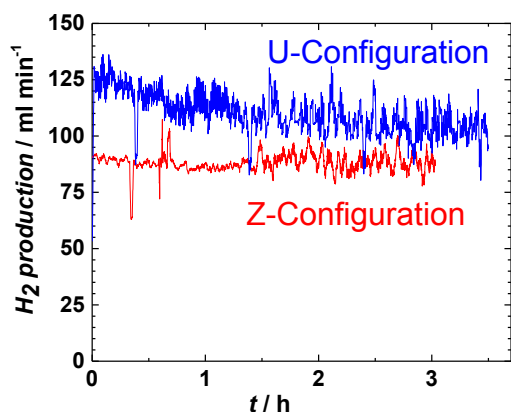


Fig. 4 The hydrogen production with different anolyte flow configurations.

The hydrogen generation profile in Fig. 4 clearly shows that the hydrogen production in the U-configuration stack is more efficient than in the Z-configuration throughout the measurement. The main reason for this is that  $\text{SO}_2$  has longer residence time in the U-configuration increasing the utilization of the  $\text{SO}_2$  reactant (Fig. 3), naturally reflecting in higher  $\text{H}_2$  production. Nevertheless, both stacks provided constant hydrogen gas production for various hours. For the day 2 the gas production had clearly decreased and was below the detection limit of the brooks instrument.

Table 1. The H<sub>2</sub> production and current efficiency of each stack configuration in comparison to a single cell experiment.

Module	H <sub>2</sub> (ml/(min x A x N cell))	Current efficiency
Stack Z	4.5	65 %
Stack U	6	85 %
Single cell	6.5	93 %

For comparison, the overall hydrogen production rate and the cell current efficiency of the different SDE stack configurations are compared with the performance of a single cell (Table 1) from previous experiments [18]. The results indicate that anolyte flow has a major influence on the current efficiency of the system and in the U-configuration the amount of H<sub>2</sub> produced increases by 40% in comparison to Z-configuration resulting in current efficiencies of 65% and 85% respectively. With the stacks the current efficiency of the single cell was not met (Table 1) dictating that further optimization of the SDE stack configuration, flows and SO<sub>2</sub> concentrations is required.

### 3.2 Unit cell performance in the stack

In order to understand the environment inside the SDE during operation, also individual unit cells in the stack were monitored. Overall, if one of the unit cells experiences harder conditions than others the coating of the bipolar plate in that particular unit cell can be modified for instance with thicker coating to ensure the increased lifetime. The voltage of each unit cell during operation for both configurations are presented in Fig 5. The cell 1/2 “in” responds to the first cell in the stack where the electrolyte flows entered the stack and the cell 5/6 “out” the last cell where the electrolyte flows exit the stack. In addition, the values of the whole stack (between plate 1 and 6) called “1/6 divided by 5” is measured but divided by 5 to provide comparable average cell voltage value.

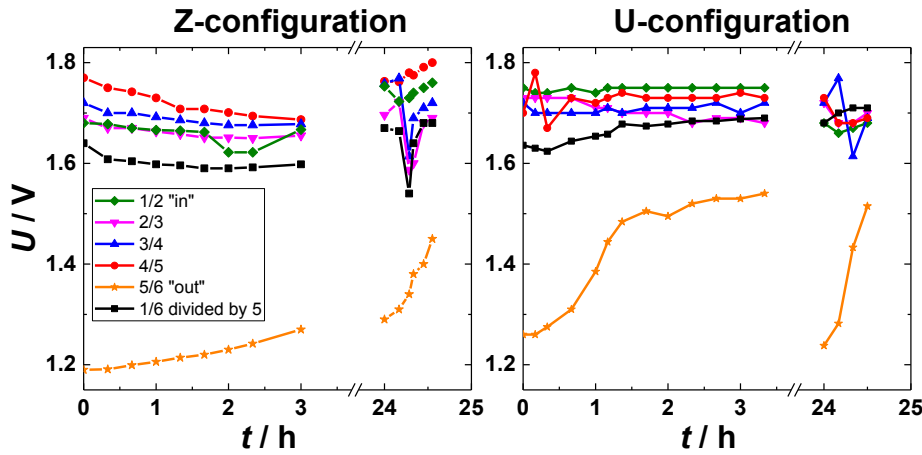


Fig. 5 Cell voltage of unit cells and the whole stack (divided with 5) at constant 4A current. Module with the Z configuration (left) and the U-configuration (right). The points correspond to actual experimental values and the lines are added as a guide for the eye.

It is evident in Fig. 5 that in both stacks the behaviour of the last cell (5/6) is clearly different in comparison to the other cells. This same phenomenon has been reported also in gas-phase electrolyser [21] as well as in PEM fuel cell [15] where it was described to be due to the pressure drop for the last cell. All the other individual cells experience steady voltages from 1.6 to 1.8 V at constant 4 A current, thus, there is no risk for the plate coating deterioration [5]. Nevertheless, the anolyte flow shows an effect on the first cell: in the Z-configuration the voltage of the first cell is lower than for the plates in the middle, however, for the U-configuration the voltage of the first cell is the highest. This could be due to the fact that in U-configuration all the anolyte is entering the first cell causing the highest liquid pressure for that cell. Similar phenomenon was reported for gas – phase electrolyser even though that most likely is utilizing the Z-configuration [21]. In both configurations the cells in the middle behave alike that is well in line what reported for the gas –phase electrolyser [21].

During the second day electrolysis (24 h after SO<sub>2</sub> feed in Fig. 5) the voltage of the unit cells is less stable. Most of the unit cells in the Z-configuration have an increase in their voltage whereas in U-configuration most of the unit cells show similar values as during the first electrolysis. For the last unit cell, the voltage continues around the same value as in the end of the first electrolysis in the Z-

configuration, however, in U-configuration the voltage of the last unit cell drops at similar value as in the beginning of the first electrolysis. But in both configurations, the voltage of the last unit cell increases clearly during the first hour and therefore the second electrolysis was executed in both cases after one hour. This less stable voltage behaviour indicates that there are reactions occurring on the bipolar plate surfaces and when the cell was disassembled visible solid sulphur on the cathode plates are observed. As was seen in Fig. 3, the  $\text{SO}_2$  concentrations at the catholyte are high and significant amount of parasitic reaction products are produced that will have an effect on the voltage of the unit cells.

In order to study the effect of the bipolar plate coating for the stacks, the electrochemical impedance spectra was performed in absence of  $\text{SO}_2$  (Fig. 6). It should be noted that the resistance in each cell at 1.5 V potential is quite high due to low activity of water electrolysis at that potential, however, this provides an opportunity to observe differences between the unit cells and the bipolar plates.

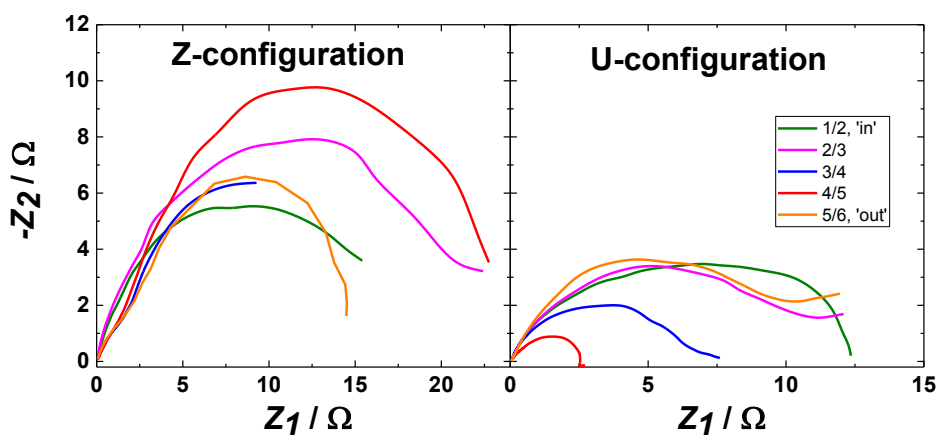


Fig. 6 Impedance at 1.5 V of the individual cells in the stack before  $\text{SO}_2$  feed (water electrolyser) for Z-configuration plates (left) and U-configuration plates (right).

For Z-configuration, the impedance of all unit cells is somewhat higher in comparison to U-configuration (Fig. 6). However, the magnitude of impedance and the shape of the Nyquist plots are similar to all unit cells. Even though there are some changes in the resistance of the unit cells, their voltage in the stack remains fairly constant (Fig. 5) indicating that small changes in the adhesion of

the bipolar plates coatings do not play a vital role in their performance. The last cells (where the electrolytes exit the cell) have the lowest cell voltage (Fig. 5) even though their resistance does not differ from the other cells (Fig. 6) implying that the different behaviour is related to the stack operation and not to the individual bipolar plate properties.

Overall, the SDE stack experiments show that the difference in bipolar plate coatings are negligible for the voltage performance of each unit cell but the anolyte flow configuration plays a vital role in SDE stack performance. The latter does not only affect the hydrogen production and the cell efficiency but also to SO<sub>2</sub> carry-over. In future, further optimization is required to reach similar current efficiency as in the case of a single cell, to hinder the SO<sub>2</sub> carry-over and to provide constant environment for individual cells in the stack for prolonging the stack lifetime.

## 4 Conclusions

To aim industrial scale H<sub>2</sub> production, efficient and cost effective alternatives are needed and SDE stack provides an interesting possibility to produce cheap, large scale H<sub>2</sub> by neutralizing SO<sub>2</sub> emissions. In this paper, an ambient pressure SDE stack with liquid electrolytes is presented. The different anolyte flow configurations (Z- and U-configurations) were tested in order to optimize the H<sub>2</sub> production of the stack. For that purpose several parameters were observed from the whole stack in order to understand the mechanisms inside the SDE during operation. According to the results, it can be observed that the U-configuration offers 40 % increased efficiency compared with the Z-configuration indicating that the anolyte flow design presents a major influence on the performance of the stack. However, the main drawback of U-configuration is the increased SO<sub>2</sub> carry-over to the cathode promoting side reaction and in long term operation lowering the stack efficiency. These both phenomena are due to larger residence time of the SO<sub>2</sub> containing electrolyte in the stack. To ensure

prolonged cell life, the environment of individual unit cells was further studied and the results imply that none of the unit cells experience high voltage that could damage the coatings on the bipolar plates. Future optimization of the stack is required to reach the efficiency of a single cell and to avoid SO<sub>2</sub> carry-over to ensure long time operation.

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