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## Introduction

To address the challenges encountered in the early stages of commercializing proton exchange membrane fuel cell (PEMFC) technology, it is essential to enhance durability and ensure reliability of fuel cells in real-world environments. Since ambient air is typically used for PEMFC operation, common airborne contaminants such as NO<sub>x</sub>, SO<sub>2</sub> and volatile organic compounds from natural and anthropogenic sources can negatively impact PEMFC performance [1]. While the performance loss can be self-recovered by operating the fuel cell with pure air, this simple procedure is not efficient for certain impurities. For instance, SO<sub>2</sub> partially reduces to elemental sulfur on the Pt surface under fuel cell operating conditions and cannot be fully removed by pure air alone [2]. Only special treatments of the contaminated cathode can lead to partial or full recovery of PEMFC performance [3-6]. This work aims to comprehensively analyze several recovery procedures for PEMFCs exposed to SO<sub>2</sub>.

## Experimental

All experiments were conducted using the HNEI segmented cell system [7]. The segmented cell system consists of the hardware, a current transducer system, and a data acquisition device. The setup is operated as a single cell using a standard fuel cell test station. The hardware contained a segmented flow field which consisted of 10 segments consecutively following the path of the 10-channel serpentine. Each segment has an area of 7.6 cm<sup>2</sup> and consisted of its own distinct current collector and GDL.

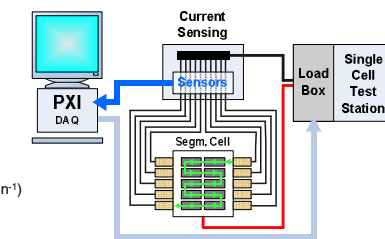
**Anode/Cathode (An/Ca) operating conditions:**  
H<sub>2</sub>/Air, 2/2 sto, 100/50%RH, 150 kPa, 80°C  
5 ppm SO<sub>2</sub>, i=0.4 and 1.0 A cm<sup>-2</sup>

## Recovery methods

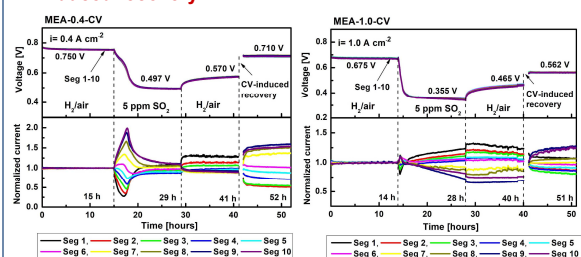
- 1. Potential cycling (CV-induced)**
  - 1) stop the load
  - 2) purge the cathode with N<sub>2</sub>
  - 3) run CV from 0.1 to 1.2 V, 10 cycles, 20 mV s<sup>-1</sup>.
- 2. O<sub>2</sub> purge recovery**
  - 1) stop the load
  - 2) purge the cathode with N<sub>2</sub> (1.5 l min<sup>-1</sup>)
  - 3) purge the cathode with pure O<sub>2</sub> (4.5 l min<sup>-1</sup>)
  - 4) repeat N<sub>2</sub> and O<sub>2</sub> purges 5 times.

## MEA properties:

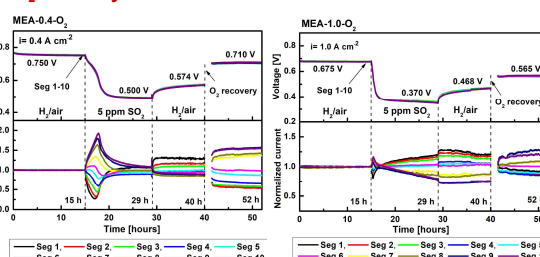
Gore, 100 cm<sup>2</sup>, 0.1/0.4 mg Pt cm<sup>-2</sup>, 25 BC, 125 μm gasket  
Cathode segmented



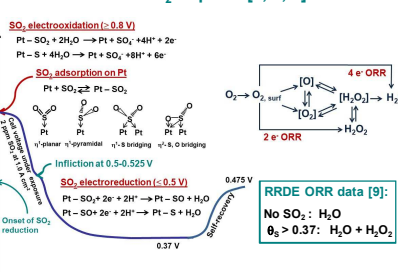
## CV-induced recovery



## O<sub>2</sub> recovery



## Mechanism of SO<sub>2</sub> impacts [2, 8, 9] and ORR



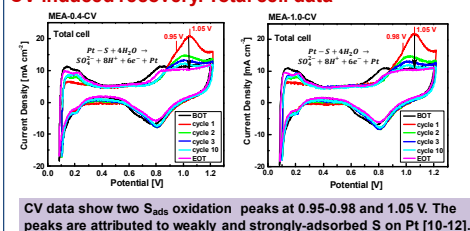
Initial cell voltage of the samples (V<sub>0</sub>) during exposure to SO<sub>2</sub> (V<sub>SO2</sub>), self-recovery (V<sub>self-rec</sub>), after recovery procedure (V<sub>rec</sub>), performance drop (ΔV) and recovery as a ratio b/w V<sub>rec</sub> and V<sub>0</sub>.

| Sample                 | i [A cm <sup>-2</sup> ] | Recovery             | V <sub>0</sub> [V] | V <sub>SO2</sub> [V] | V <sub>self-rec</sub> [V] | V <sub>rec</sub> [V] | ΔV [mV] | Recovery [%] |
|------------------------|-------------------------|----------------------|--------------------|----------------------|---------------------------|----------------------|---------|--------------|
| MEA-0.4-CV             | 0.4                     | CV                   | 0.750              | 0.497                | 0.570                     | 0.710                | 40      | 95           |
| MEA-1.0-CV             | 1.0                     | CV                   | 0.675              | 0.355                | 0.465                     | 0.562                | 105     | 84           |
| MEA-0.4-O <sub>2</sub> | 0.4                     | O <sub>2</sub> purge | 0.750              | 0.500                | 0.574                     | 0.710                | 40      | 95           |
| MEA-1.0-O <sub>2</sub> | 1.0                     | O <sub>2</sub> purge | 0.675              | 0.468                | 0.468                     | 0.565                | 110     | 84           |

1. The injection of SO<sub>2</sub> caused a decrease in voltage response with inflection point.
2. SO<sub>2</sub> impact depended on operating voltage/current.
3. At the steady state, cell voltage was 0.497-0.500 V for 0.4 A cm<sup>-2</sup> and 0.355-0.370 V for 1.0 A cm<sup>-2</sup>.
4. Operation in pure air resulted in partial recovery.
5. CV-induced and O<sub>2</sub> recovery procedures revealed the same results: 95% recovery for 0.4 A cm<sup>-2</sup> and 84% for 1.0 A cm<sup>-2</sup>.

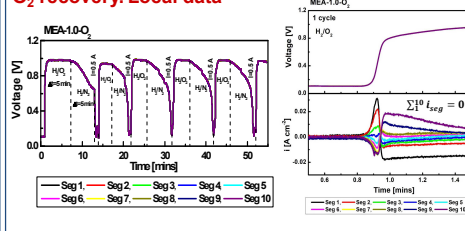
1. SO<sub>2</sub> in air stream adsorbed on Pt and caused a decrease in available ECA and shift of ORR mechanism from 4 e<sup>-</sup> to 4 + 2 e<sup>-</sup>.
2. Adsorption of SO<sub>x</sub> led to voltage drop and local current redistribution.
3. Electroreduction of SO<sub>x</sub> occurs at low potentials (< 0.5 V) with the formation of S<sup>0</sup>.
4. To ensure full recovery, the cathode potential had to be high enough (>0.9-1.0 V) to oxidize S<sup>0</sup> to soluble products.

## CV-induced recovery. Total cell data



CV data show two S<sub>2</sub>O<sub>6</sub> oxidation peaks at 0.95-0.98 and 1.05 V. The peaks are attributed to weakly and strongly-adsorbed S on Pt [10-12].

## O<sub>2</sub> recovery. Local data

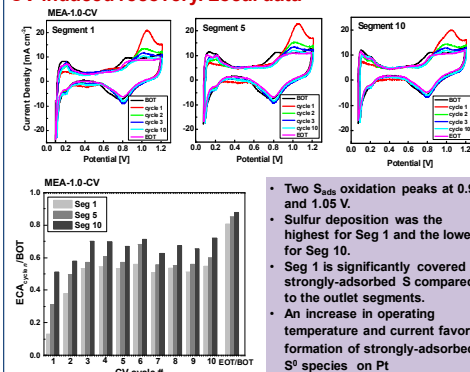


- The positive currents at Seg 1-4 indicated that the regular fuel cell reactions, ORR and HOR, occurred at the cathode and anode, respectively.
- Negative current indicated oxidation reactions at the cathode (either oxygen evolution, carbon corrosion or sulfur oxidation).
- Current density generated by sulfur oxidation was ~10-15 mA cm<sup>-2</sup> and could have been overlapped by larger currents produced at the start-up.

## Conclusion

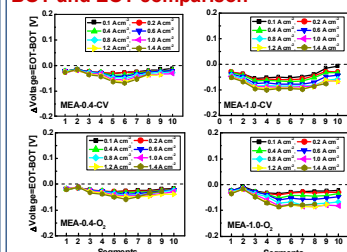
- To remove S-containing species, the electrode potential needs to be increased to values where electrooxidation of SO<sub>2</sub> and S<sup>0</sup> can occur, >0.8-0.9 V.
- The work evaluated the effectiveness of two recovery methods: potential cycling and O<sub>2</sub> purge.
- The potential cycling at the cathode was performed from 0.1 to 1.2 V vs potential at the anode and at H<sub>2</sub>/N<sub>2</sub> gas configuration for anode/cathode, respectively.
- The O<sub>2</sub> recovery procedure includes repetitive variation of cathode feed gas from N<sub>2</sub> to O<sub>2</sub> at a flow rate of 4.5 l min<sup>-1</sup>, which ensures potential variation at the cathode from 0.1 to 0.98-0.99 V.
- The results demonstrated that both methods achieved substantial recovery of the cell performance, with up to 95% recovery efficiency for fuel cells contaminated at lower current densities (0.4 A cm<sup>-2</sup>) and 84% at higher current densities (1.0 A cm<sup>-2</sup>).
- O<sub>2</sub> purge technique seems to be more suitable for practical operation. The O<sub>2</sub> purge recovery does not require auxiliary equipment and can be applicable for field operation.

## CV-induced recovery. Local data



- Two S<sub>2</sub>O<sub>6</sub> oxidation peaks at 0.95 and 1.05 V.
- Sulfur deposition was the highest for Seg 1 and the lowest for Seg 10.
- Seg 1 is significantly covered by strongly-adsorbed S compared to the outlet segments.
- An increase in operating temperature and current favors formation of strongly-adsorbed S<sup>0</sup> species on Pt

## BOT and EOT comparison



The performance drop was attributed to an increase in activation and mass transport losses. An increase in activation overpotential (25-30 mV) was connected to the drop in the cathode ECA, while the mass transport losses (~5-80 mV) originated from degradation of the catalyst layer and GDL under SO<sub>2</sub> exposure.

- The current density of SO<sub>2</sub> exposure determined the final performance after the recovery.
- The cell contamination to SO<sub>2</sub> at 0.4 A cm<sup>-2</sup> affected the middle part of MEAs more (70 mV) compared to the inlet and outlet (10-30 mV).
- Operation of the MEAs and exposure to SO<sub>2</sub> at 1.0 A cm<sup>-2</sup> led to a performance drop of 30-50 mV for the inlet Seg 1-3, while Seg 4-8 demonstrated a voltage loss of 50-95 mV for MEA-1.0-CV and 30-85 mV for MEA1.0-O<sub>2</sub>.

## BOT and EOT ECA of the samples.

| Sample                            | Anode ECA [m <sup>2</sup> g <sup>-1</sup> ] |      | Cathode ECA [m <sup>2</sup> g <sup>-1</sup> ] |      | ΔECA [%] |         |
|-----------------------------------|---------------------------------------------|------|-----------------------------------------------|------|----------|---------|
|                                   | BOT                                         | EOT  | BOT                                           | EOT  | anode    | cathode |
| MEA-0.4-CV                        | 84.3                                        | 71.2 | 66.6                                          | 53.6 | 15.7     | 19.5    |
| MEA-1.0-CV                        | 91.1                                        | 78.8 | 67.5                                          | 52.1 | 13.5     | 22.9    |
| MEA-0.4-O <sub>2</sub>            | 95.9                                        | 81.6 | 68.3                                          | 56.2 | 14.9     | 17.7    |
| MEA-1.0-O <sub>2</sub>            | 95                                          | 82.1 | 69.6                                          | 56.8 | 13.6     | 18.3    |
| Reference, 1.0 A cm <sup>-2</sup> | 70.5                                        | 67.4 | 65.6                                          | 57.7 | 4.4      | 12.0    |

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