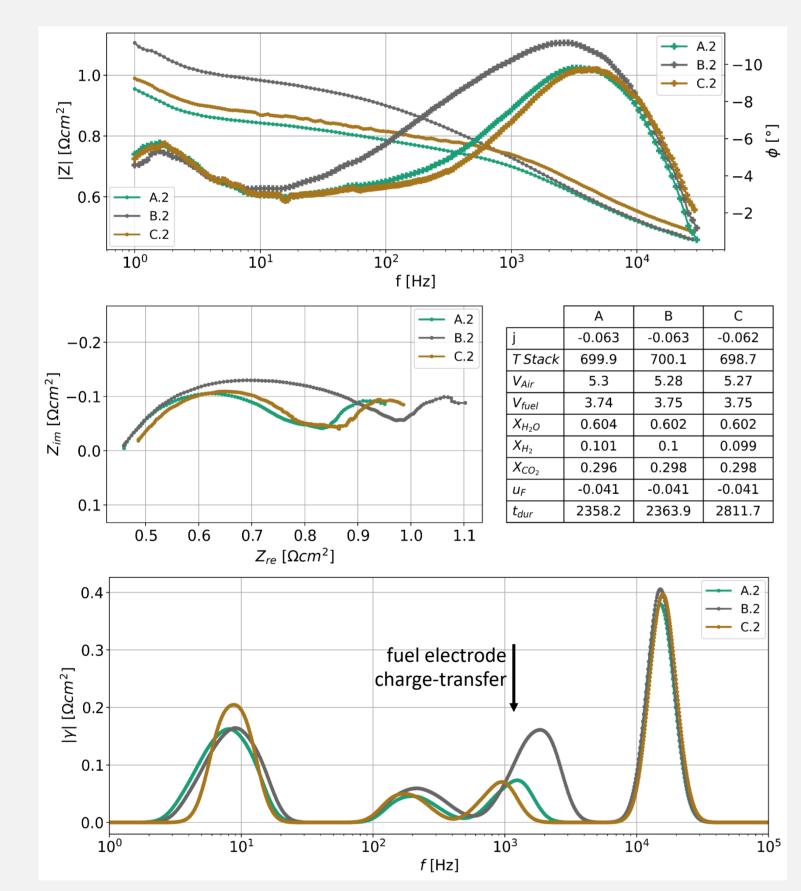
The biogas-oxyfuel process as a carbon source for high-temperature co-electrolysis and degradation by oxidized sulphur contaminants



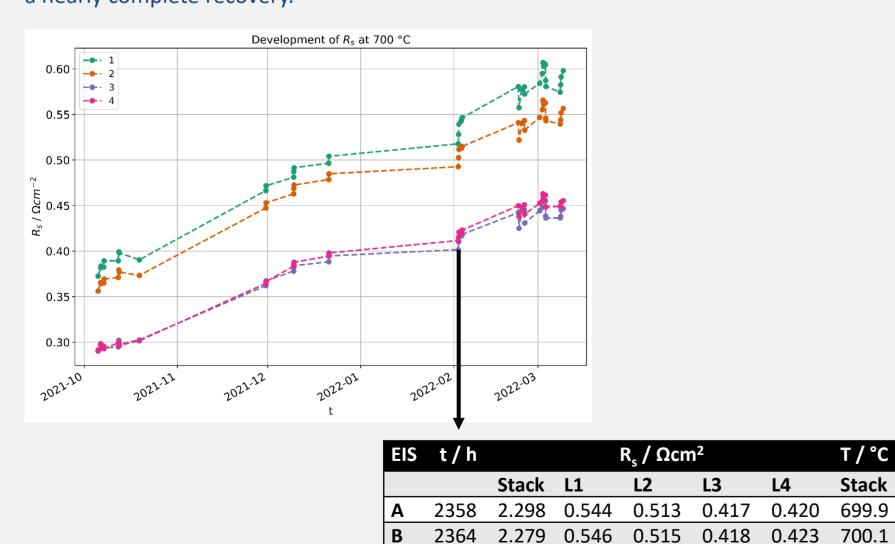
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Introduction & Concept Scheme Co-Electrolyzei $H_2 + CO$ Fermenter **CHP** PtX process H_2O O_2 Biogas contains a lot of CO₂, often not directly usable for many processes Experiment with an F10 short-stack with four F1004 repeating units each containing a single Exemplary composition: ■ 59% CH₄, 40.4% CO₂, 0.6% O₂ Ni/YSZ supported cell (Ni/YSZ fuel electrode, YSZ electrolyte, LSFC air electrode) 0-5 ppm H₂S 49% H₂O Upgrading of biogas not always economically feasible due to small plant Assuming the total oxidation of biogas by pure H_2O oxygen and formation of SO₂ to generate feed 0.71 ppm SO₂ Use as-is to generate heat with oxyfuel process SO_2/N_2 Use exhaust gas as point-source of CO₂ and use it as carbon source H_2O/CO_2 ratios of 1.2 to 2.0 with 10% H_2 in (50ppm) Use oxygen for the oxyfuel process feed at 700 - 790 °C and current densities of 0 41% CO₂ Relevant sulphur species for co-electrolysis feed is SO₂ or 0.75 Acm⁻² with a net conversion ratio of ■ Heterogenous reduction of SO₂ with H₂ or CO is catalyzed by oxides like 10% H₂ SO₂ introduced by a premixed and calibrated YSZ or CeO₂ ■ Intermediary steps and side products beside H₂S can include significant mixture of 50 ppm SO₂ in N₂ amounts of elemental S and COS depending on process conditions

EIS Characterization



EIS spectra recorded before (A.2, only layer 2 shown) and after (B.2) a poisoning experiment (0.71 ppm SO₂, without external polarization except of the intermittent EIS measurements) showed a severe impact on the high-frequency part of the spectrum. The corresponding DRT deconvolution (calculated by DRTtools) showed the damage to concentrate mainly on the peak usually attributed to the fuel electrode charge-transfer process. A spectrum recorded ~450 h later (C.2) showed a nearly complete recovery.



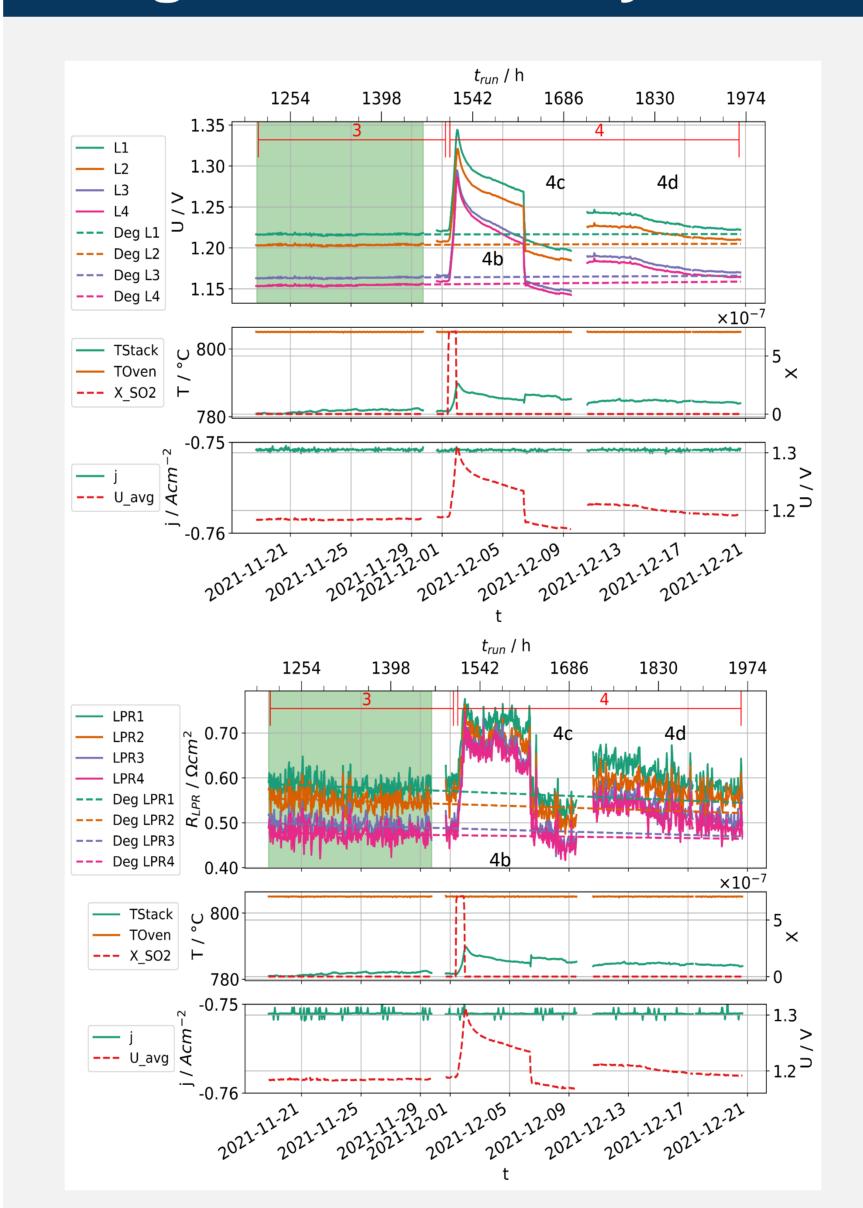
The modelled high-frequency series resistance (R_s, "ohmic resistance") is not visible in the DRT deconvolution and given in the table for the EIS measurements described above. Its development for all four layers during the overall stack experiment is shown for comparison. No significant increase of R_s was observed around the poisoning (A, B) while the increase at C likely reflects the usual degradation during stationary co-electrolysis.

2812 2.357 0.581 0.541 0.442 0.450 698.7

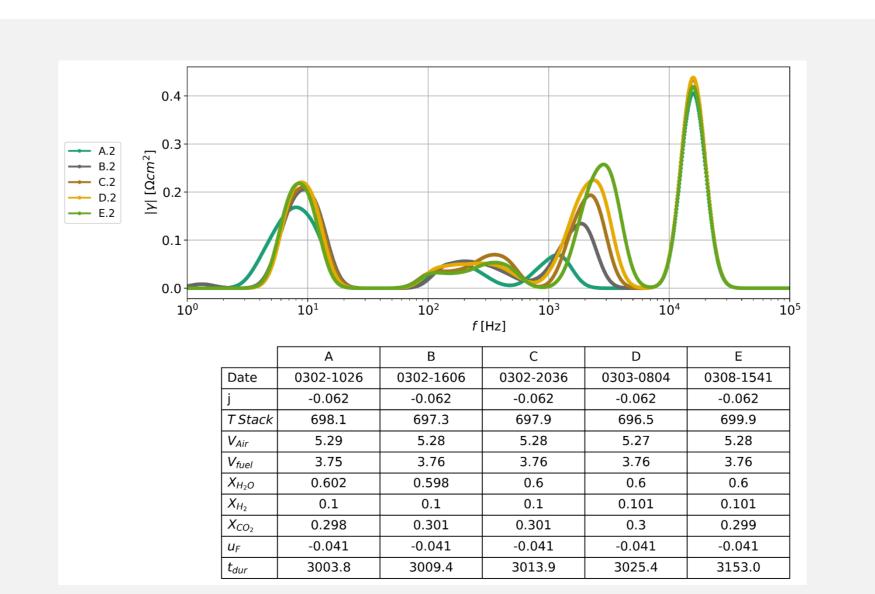
T/°C

A second set of EIS spectra recorded during and after another poisoning experiment is shown to the right. B.2 and C.2 show the degradation during the poisoning compared to the spectrum recorded directly before (A.2) and similar changes as above were observed. Interestingly, peak likely associated with transport processes in the fuel and air electrodes is splitting in two and one of them increases slightly, attributing it to the fuel electrode. After the conclusion of SO₂ dosage (D.2, E.2), no electrolysis operation was conducted and the peak associated to charge-transfer processes continued to increase for ~140 h, suggesting the external polarization to be an important factor for the recovery observed above.

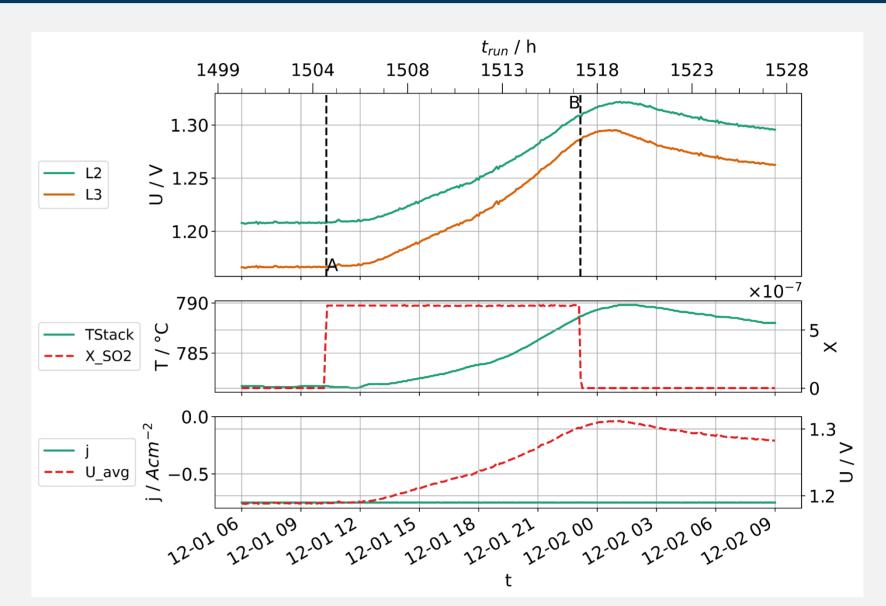
Long-term Recovery



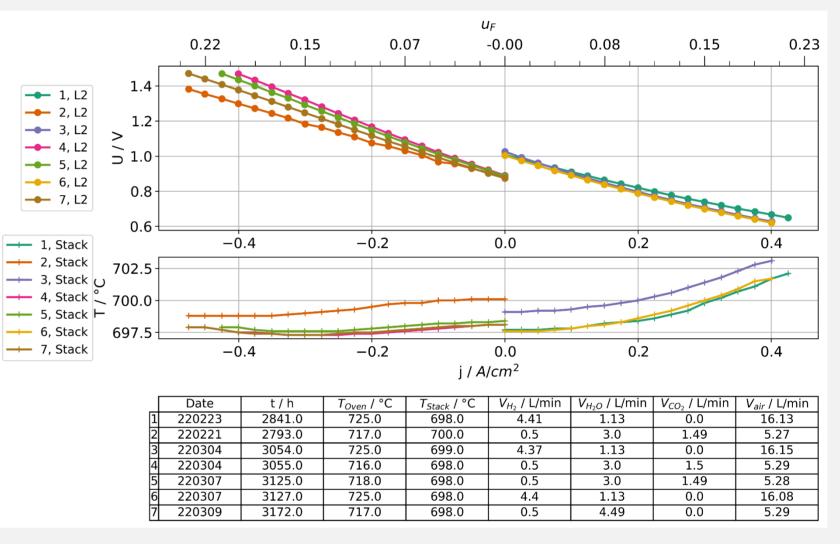
Observation of cell voltages and instantaneous cell resistances at the operating point (measured by the LPR method). Following a stable stationary co-electrolysis operation (time span 3) with 5 mΩcm²kh⁻¹ this shows a poisoning experiment and its subsequent long drawn-out recovery over ~450 h. During recovery, coelectrolysis (4b, H₂O/CO₂ ratio of 1.2), steam electrolysis (4c) and co-electrolysis (4d, H₂O/CO₂ ratio of 2.0) were performed to look for significant changes of behaviour. After 450 h an extensive recovery was observed.



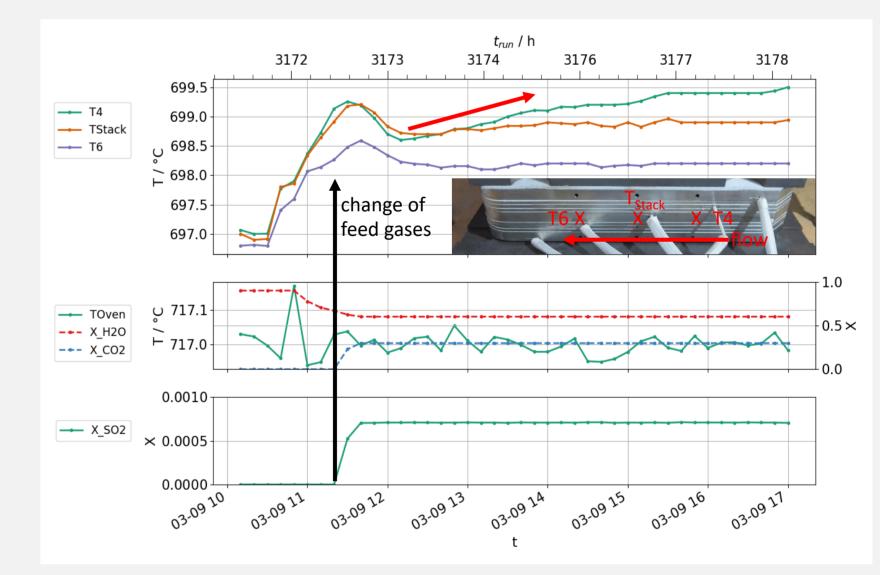
Short-term Poisoning



Dosage of 0.71 ppm SO2 to the feed (A) during stationary operation (0.5 Acm⁻², CR 50%, H₂O/CO₂ ratio of 1.2) caused severe degradation 1-2 h later, expressed by cell voltages and stack temperature. Stabilization occurred ~2 h after termination of dosage, followed by slow recovery.



U-j curves in fuel-cell and co-electrolysis mode before (1, 2) and after (3, 4) showed a strong increase in cell resistances, corresponding to an increase of ~20% in fuelcell mode and ~40% in co-electrolysis mode (at 0.4 Acm⁻²). After ~70 h of standby at OCV (5, 6) an extensive recovery in fuel-cell mode, but a much less pronounced recovery in co-electrolysis mode was observed. Curve 7 shows a comparison to steam electrolysis mode ~45 h later. An EIS spectrum during this time showed no improvement yet in co-electrolysis mode, which could indicate a less severe impact in steam electrolysis mode.



Observation of the stack temperatures during SO2 dosage without any external polarization shows first a decrease of temperatures due to cooling by the reverse water-gas shift reaction. Shortly after, a slow increase can be observed at the sensor nearest to the feed gas inlet and less pronounced at the sensor near the cell centre. This is interpreted as a sign of impaired kinetics of the heterogenous watergas shift reaction, catalysed on nickel surfaces. Since this an important reaction coupled to the electrolytic steam conversion in co-electrolysis mode, it may explain an even greater impact in co-electrolysis mode.

Conclusions & Outlook

- Heavy impact of 0.7 ppm SO₂ in feed-gases within < 12 h observed
- Slow recovery during stationary operation with clean feed-gases observed according to
- cell voltages and resistances Confirmed in repeated experiments with EIS
- Charge-transfer in fuel electrode seriously degraded
- No impact on HF series resistance ("ohmic resistance")
- Recovery likely dependent on external polarization ■ Reverse water-gas shift reaction inhibited → possible explanation for more serious impact on electrolysis U-j curve
- Despite recovery, the operation on oxyfuel exhaust gases requires thorough sulphur removal or possibly very clean feedstocks for biogas fermentation.
- Next steps planned: lower sulphur contents to narrow down technical requirements, further investigation of recovery and dependence on operation conditions

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