Supplementary Materials for

Electrolysis of sulfur waste to capture and store CO_2

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References (1)

Methods

Mg^{2+}-blocking membrane synthesis

The membrane modifications were performed in a beaker containing the reagents, leading to a two-step modification. The protons of the Nafion™ membrane were first ion-exchanged with protonated aniline using a 1 vol% aniline in 1 M HCl aqueous solution. After rinsing, the beaker was then filled with a 0.2 M $K_2S_2O_8$ aqueous solution to induce the polymerization for 1 hour. The Mg^{2+} blocking membranes were stored in 1 M HCl for a minimal 24 hours prior to use.

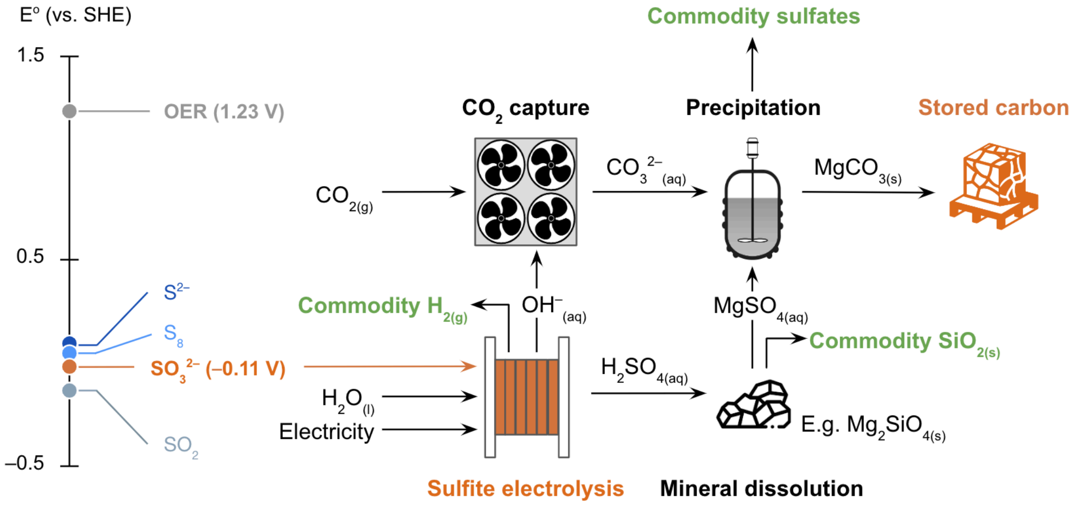
Anode preparation

To fabricate carbon composite electrodes for sulfite electrolysis, a catalyst ink was prepared by mixing 8 mg of 50% Pt 50% HSA Ketjenblack and 8 μL of D2020 Nafion dispersion (20% wt) in 8 mL of ethanol. The catalyst ink was then deposited on the Freudenberg H23 carbon paper using a commercial gravity-fed pneumatic spray-coater to make the electrode (geometric area: 4 cm^2) with Pt loadings of 1 ± 0.1 mg cm^{-2}.

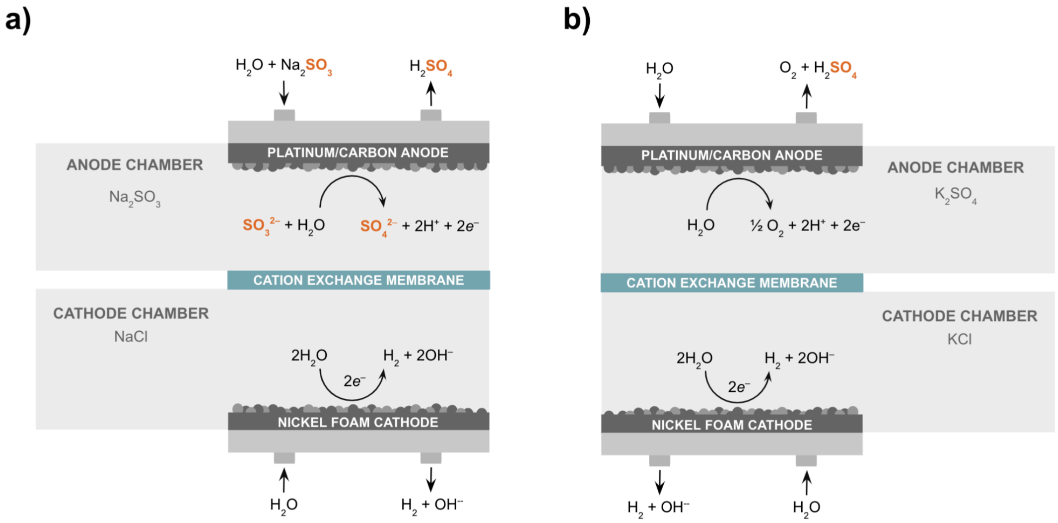
Precipitate characterization

Scanning electron microscopy (SEM) was performed using a FEI Helios NanoLab 650 dual beam scanning electron microscope with an accelerating voltage of 5.0 keV and a beam current of 50 pA.

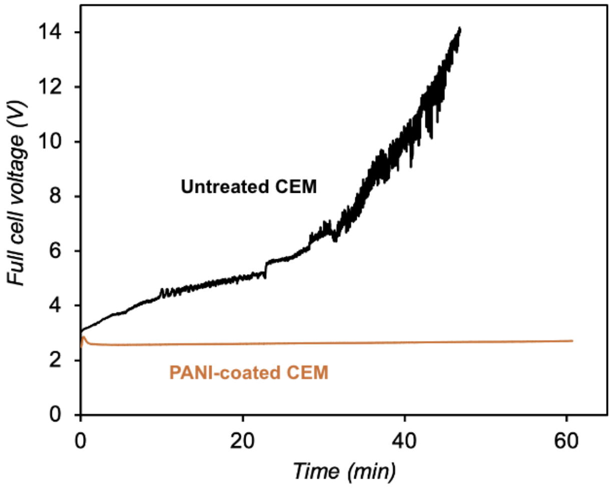
Powder X-ray diffraction (XRD) was performed using a Rigaku SmartLab instrument with a PhotonMax high-flux 9 kW rotating anode X-ray source. Highscore (Plus) search-and-match was used for peak analysis.



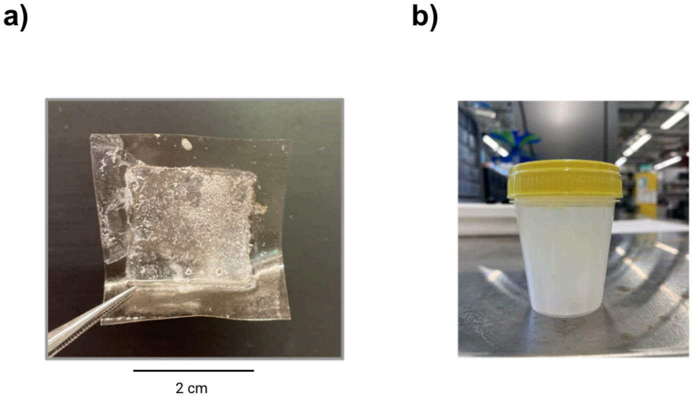
Supplementary Fig. 1. Sulfur waste to drive carbon capture and storage. Standard potentials for sulfur compounds (left) and process diagram of CO_2 capture and storage using sulfite (right).



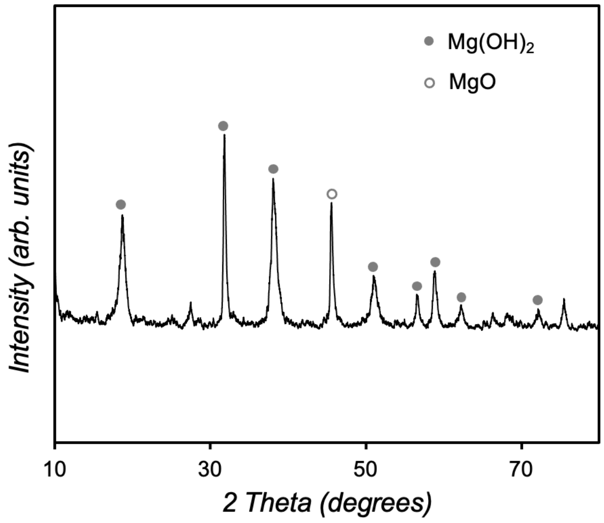
Supplementary Fig. 2. Schematic representation of a) the sulfite electrolyzer and b) water electrolyzer used in this study.



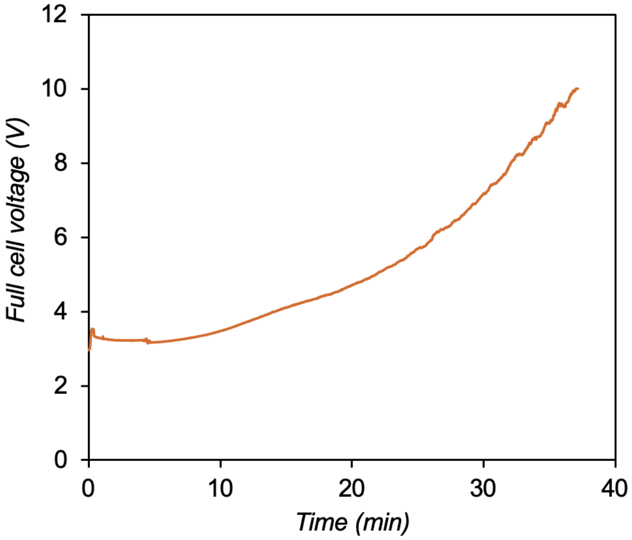
Supplementary Fig. 3. Membrane voltage and ion transport. (**A**) Full cell voltage of the sulfite electrolyzer during electrolysis at 100 mA cm^{-2} with an anolyte containing 0.1 M SO_3^{2-} and 30 g L^{-1} of milled Mg_2SiO_4. This experiment was conducted with an untreated CEM (black) and a PANI-coated CEM (orange).



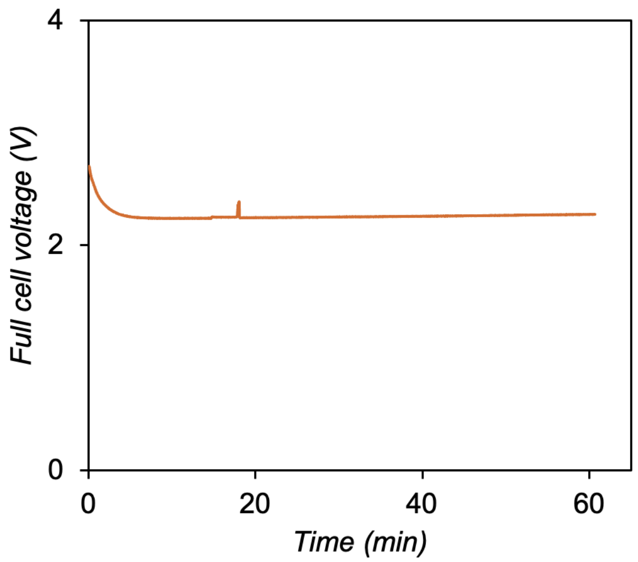
Supplementary Fig. 4. a) Unmodified Nafion CEM and b) catholyte after 60 minutes of electrolysis at 100 mA cm^{-2} in the sulfite electrolyzer using an anolyte containing 30 g L^{-1} Mg_2SiO_4.



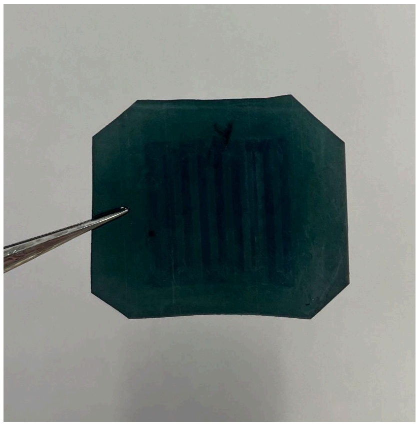
Supplementary Fig. 5. Powder XRD of the precipitate collected on the cathode-facing side of the Nafion CEM following electrolysis at 100 mA cm^{-2} when 30 g L^{-1} of Mg_2SiO_4 was added to the anolyte of the sulfite electrolyzer containing 0.1 M SO_3^{2-}. The solids observed were primarily $Mg(OH)_2$ and MgO.[1]



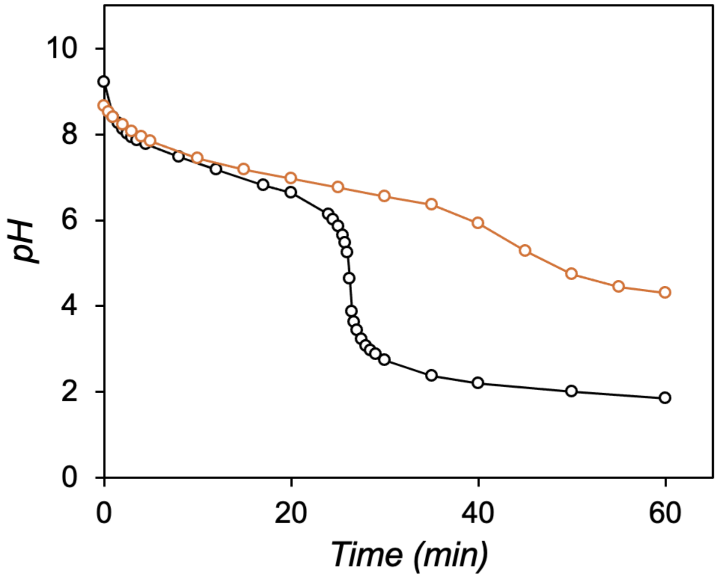
Supplementary Fig. 6. E_{cell} of the sulfite electrolyzer during electrolysis at 100 mA cm^{-2} when 0.5 M of $MgSO_4$ is added to the anolyte solution containing 0.1 SO_3^{2-}.



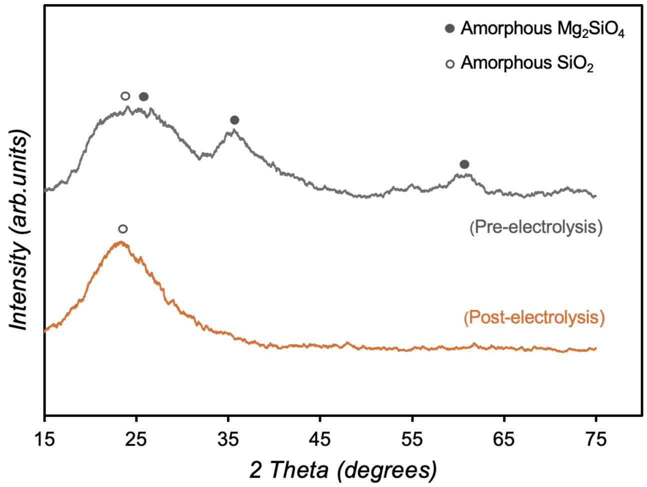
Supplementary Fig. 7. E_{cell} of the sulfite electrolyzer during electrolysis at 100 mA cm^{-2} using a PANI-modified CEM. The catholyte consisted of 1.0 M NaCl and the anolyte consisted of 0.1 M Na_2SO_3.



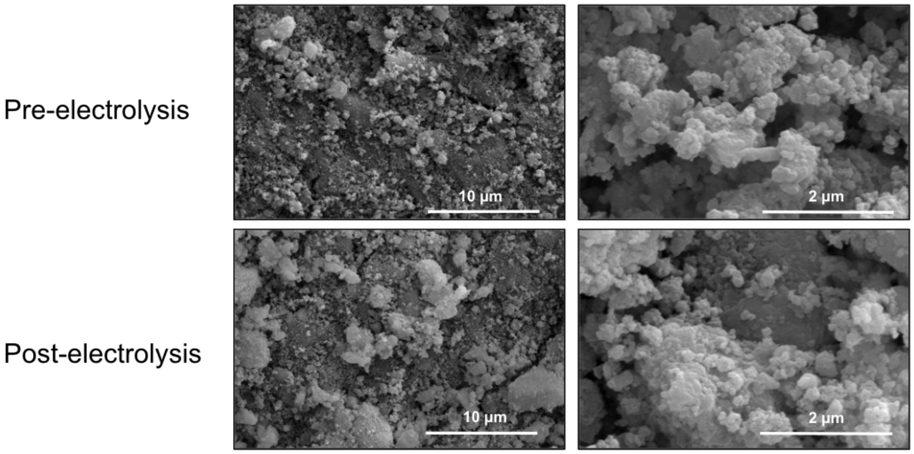
Supplementary Fig. 8. PANI-modified Nafion CEM following electrolysis experiments performed at 100 mA cm^{-2} and with anolyte containing 30 g L^{-1} of Mg_2SiO_4.



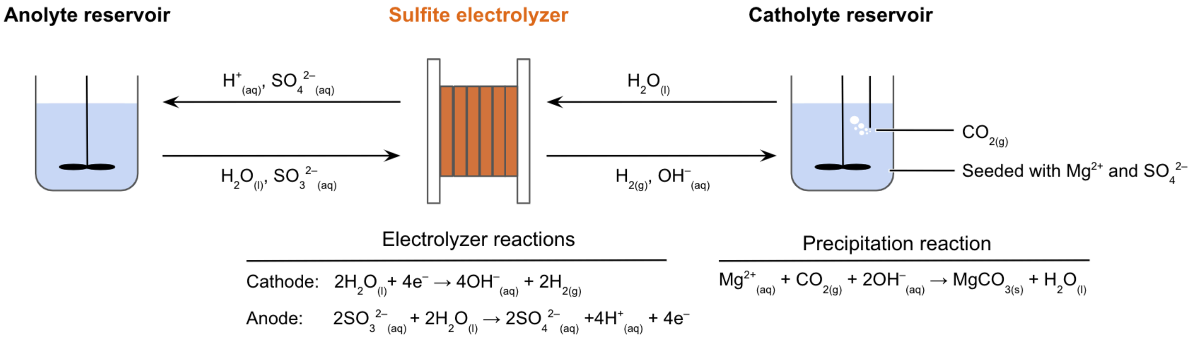
Supplementary Fig. 9. Anolyte pH on the sulfite electrolyzer during 60 minutes of electrolysis at 100 mA cm^{-2}. Experiments were conducted without Mg_2SiO_4 (black) and with 30 g L^{-1} Mg_2SiO_4 (orange) in the anolyte.



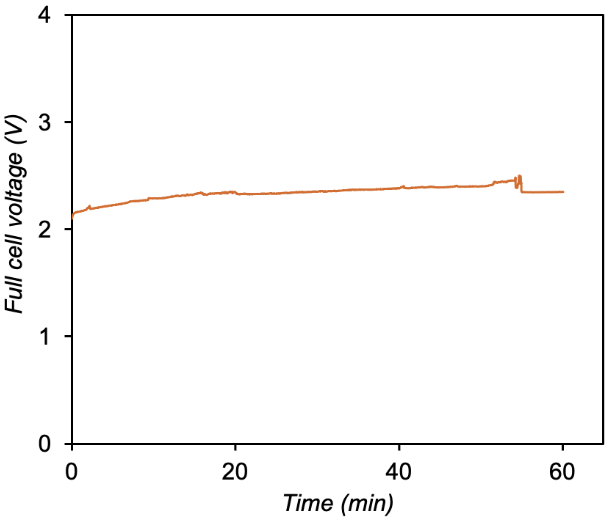
Supplementary Fig. 10. Powder XRD diffractograms of the solid pre-electrolysis (gray) and post-electrolysis (orange) of electrolysis at a constant applied current density of 200 mA cm^{-2}. The anolyte in this experiment was prepared by adding 5 g L^{-1} of milled Mg_2SiO_4 to a solution containing 0.2 M SO_3^{2-}. This solution was fed into the electrolyzer during 60 minutes of electrolysis at a flow rate of 100 mL min^{-1}. The anolyte reservoir was stirred continuously.



Supplementary Fig. 11. SEM images of the solid present in the anolyte before (top panels) and after (bottom panels) electrolysis at 100 mA cm^{-2} for 60 minutes. The anolyte consisted of 5 g L^{-1} Mg_2SiO_4 and 0.1 M Na_2SO_3.



Supplementary Fig. 12. Setup for CO_2 capture and mineralization in the sulfite electrolyzer. The electrolyzer is supplied with a 1.0 M NaCl solution seeded with 0.5 M $MgSO_4$ to the cathode chamber. This solution is contained in a reservoir that is bubbled with CO_2 during electrolysis and serves as the precipitation reactor. The anode chamber of the electrolyzer is supplied with a 1.0 M Na_2SO_3 solution which is recirculated from a reservoir.



Supplementary Fig. 13. E_{cell} of the integrated sulfite electrolyzer during electrolysis at 100 mA cm^{-2}. The anolyte consisted of 1.0 M Na_2SO_3. The catholyte consisted of 1.0 NaCl and 0.5 M of $MgSO_4$. CO_2 was bubbled into the catholyte to maintain a pH between 9.5–10.

Supplementary Table 1. Experimental Energy Intensities of the Integrated Sulfite Electrolyzer

Exp. no.	*j (mA cm^{-2})*	*Voltage (V)*	*Mineralization rate (10^{-6} mol min^{-1})*	*Energy Intensity (MWh ton^{-1} CO_2)*
1	100	2.2	50.7	6.5
2	100	2.3	24.2	13.8
3	100	2.2	61.6	5.4
4	200	2.8	95.4	8.9
5	200	3.1	100.8	9.4
6	200	2.8	76.1	11.2
7	400	4.2	132.9	19.2
8	400	3.7	193.2	11.6
9	400	3.8	96.6	23.8

Supplementary Note 1.

Energy intensity of captured CO_2 using the sulfite electrolyzer (from exp. no. 3 from table S1.)

$$P_{electrolyzer} = E_{cell} \cdot j \cdot A_{elec} = (2.2\ V)\left(0.1\ A/cm^2\right)\left(4\ cm^2\right) = 0.00088\ kW$$

$$m_{CO2} = (0.51\ g_{\ MgCO3\cdot 3H2O})(44.01\ g/mol)/(138.4 g/mol) = 0.162\ g$$

$$MWh/ton\ of\ CO_2 = (1000000\ g\ /m_{CO2})(P_{electrolyzer})/(1000\ kWh/MWh)(1\ h)$$

$$MWh/ton\ of\ CO_2 = (1000000\ g\ /\ 0.162\ g)(0.00088\ kWh)/(1000\ kWh/MWh)(1\ h)$$

$$= 5.43\ MWh/ton\ of\ CO_2$$

Supplementary Note 2.

Cost per ton of captured CO_2 using the sulfite electrolyzer (from exp. no. 3 from table S1.)

Assumed electricity cost of \$ 0.03 kWh^{-1}

$$P_{electrolyzer} = E_{cell} \cdot j \cdot A_{elec} = (2.2\ V)\left(0.1\ A/cm^2\right)\left(4\ cm^2\right) = 0.00088\ kW$$

$$m_{CO2} = (0.51\ g_{\ MgCO3\cdot 3H2O})(44.01\ g/mol)/(138.4 g/mol) = 0.162\ g$$

$$\$/ton\ of\ CO_2 = (1000000\ g\ /\ 0.162\ g)(0.00088\ kWh)(\$0.03\ \ kWh^{-1}) = \$162$$

Supplementary Note 3.

Theoretical maximum carbon storage rate at 100 mA cm^{-2}

$$mol_{OH-} = C \cdot A \cdot V \cdot t\ /\ N_{A\cdot j}$$

$$mol_{OH-} = (6.24E18\ e^{-})(0.4\ A)(0.1\ L)(3600\ s)/(6.022E - 23\ mol^{-1}) = 0.0149\ mol$$

$$mol_{carbonate} = 0.5\ \cdot mol_{OH-} = 0.0075\ mol$$

$$mol_{nesquehonite} = mol_{carbonate} = 0.0075\, mol$$

$$Carbon\ storage\ rate = (0.0075\, mol) / (60\, min) = 1.25E - 4\, mol\, min^{-1}$$

References

1. Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr B Struct Sci Cryst Eng Mater* **72**, 171–179 (2016).