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Supporting Information

Formate Over-Oxidation Limits Industrialization of Glycerol Oxidation Paired with Carbon Dioxide Reduction to Formate

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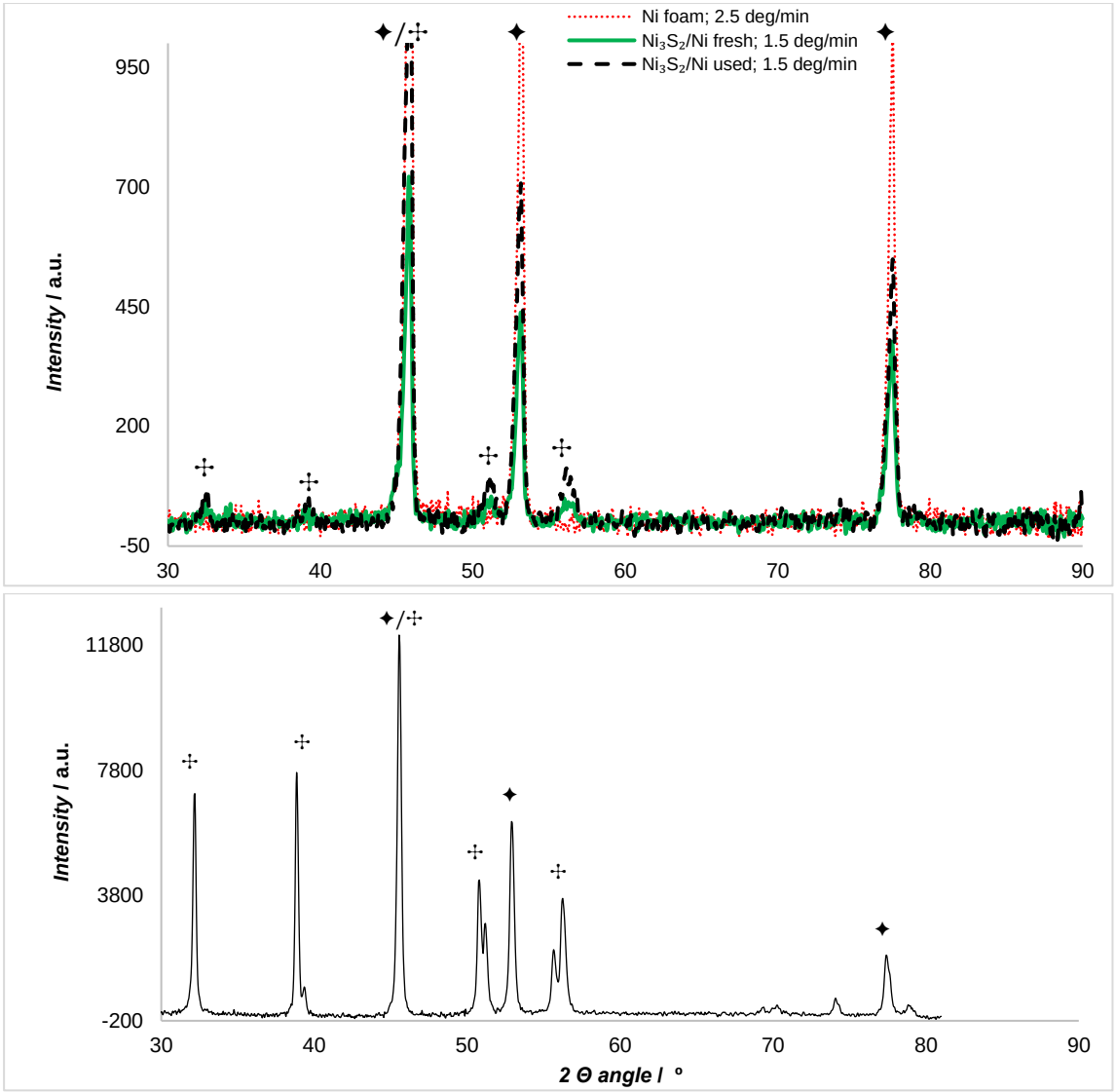
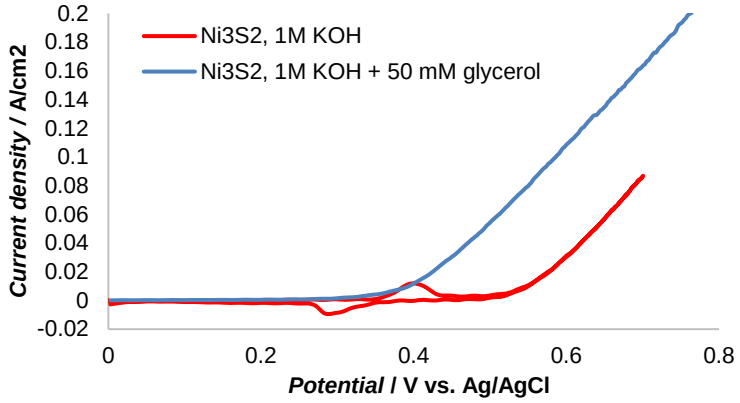
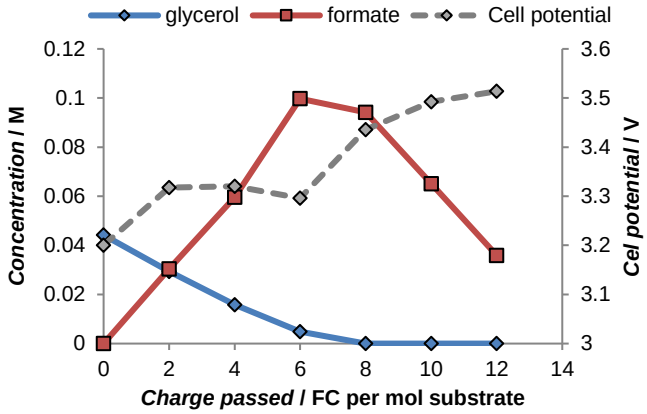


SI 1. Top graph: XRD measured on freshly prepared Ni_3S_2/NF anodes and on Ni_3S_2/NF anode after performed > 10 hours electrolysis. Bottom graph: XRD obtained from a powdered Ni_3S_2 anode. ✣: signal corresponding to Ni_3S_2. ✦: signal corresponding to nickel



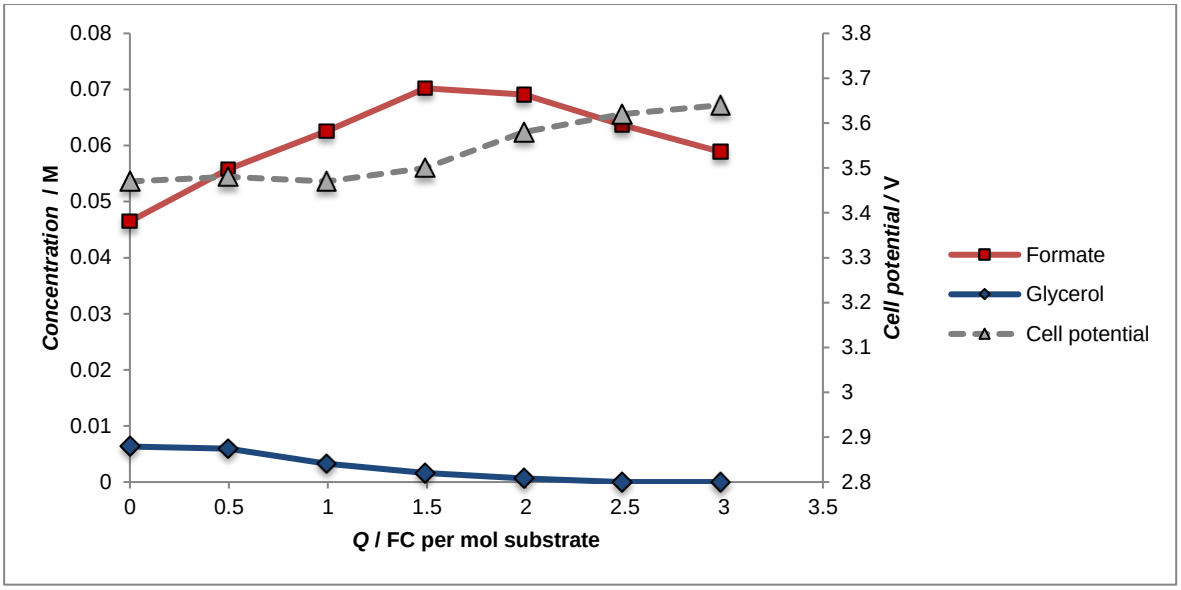
SI 2. CV with Ni_3S_2/NF working electrode (υ = 5 mV/s) in 1 M KOH (red line). Linear sweep voltammograms with 0.05 M glycerol (blue line)



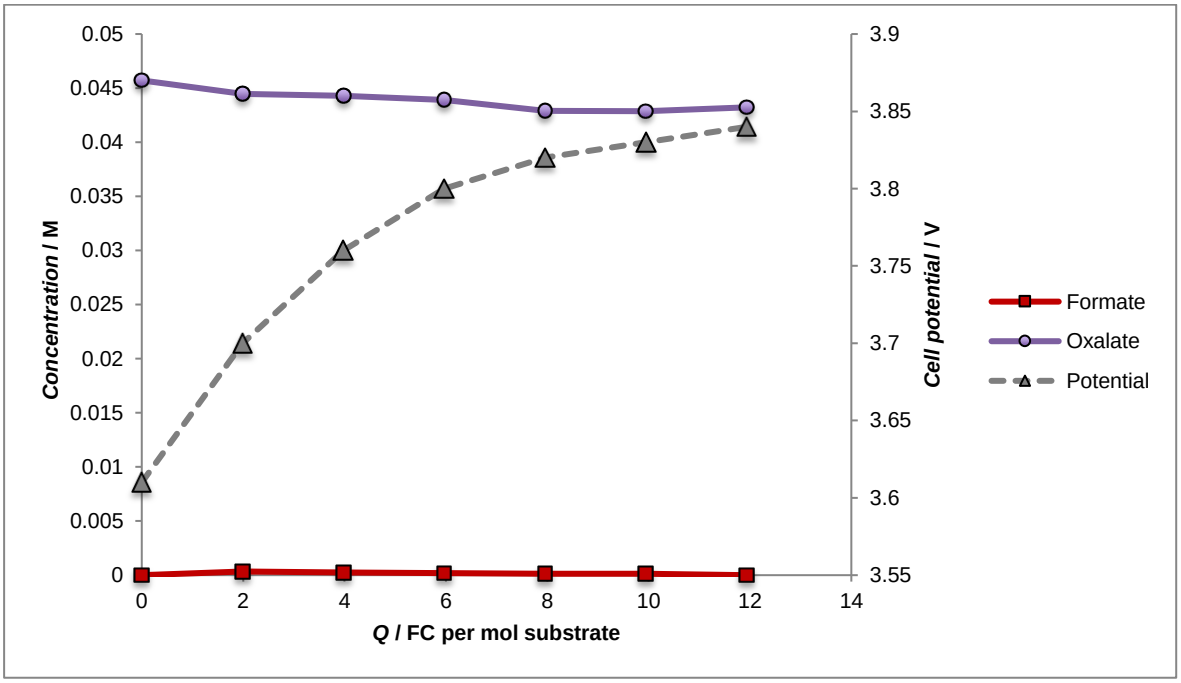
SI 3. Concentration profile and cell potential during electrolysis of glycerol with Ni_3S_2/NF anodes with 100 mA/cm^2 and targeted starting concentration of glycerol of 50 mM. A theoretical conversion of 100% corresponds to the passing of 8 FC/mol of charge. This equals 2 hours at 40 minutes reaction time.

$$Faraday\ efficiency\ (\%) = \frac{\frac{[formate]}{3} \cdot V_{anolyte}}{\frac{i}{nF} \cdot t} * 100 \qquad \text{(Equation 1)}$$

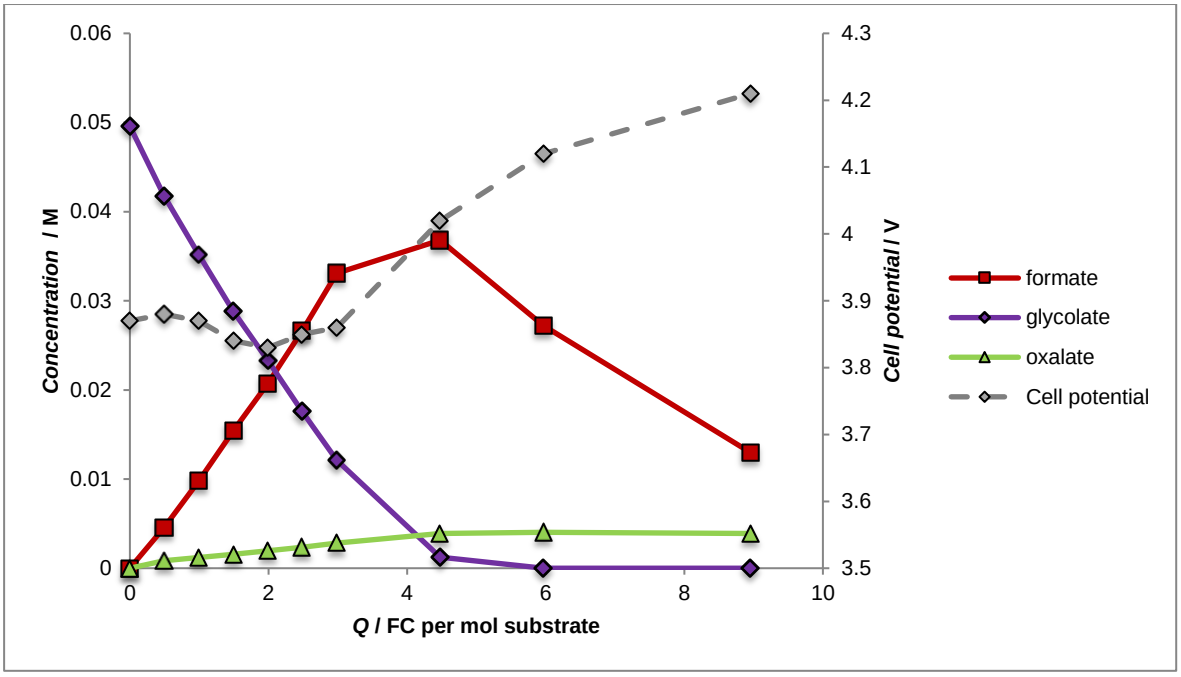
SI 4. Equation for calculation the Faraday efficiency to formate. [formate] = formate concentration (M) at time t (s). $V_{anolyte}$ = volume of the anolyte (L), i = current (A), n = number of electrons involved in the oxidation, F = Faraday's number (96485).



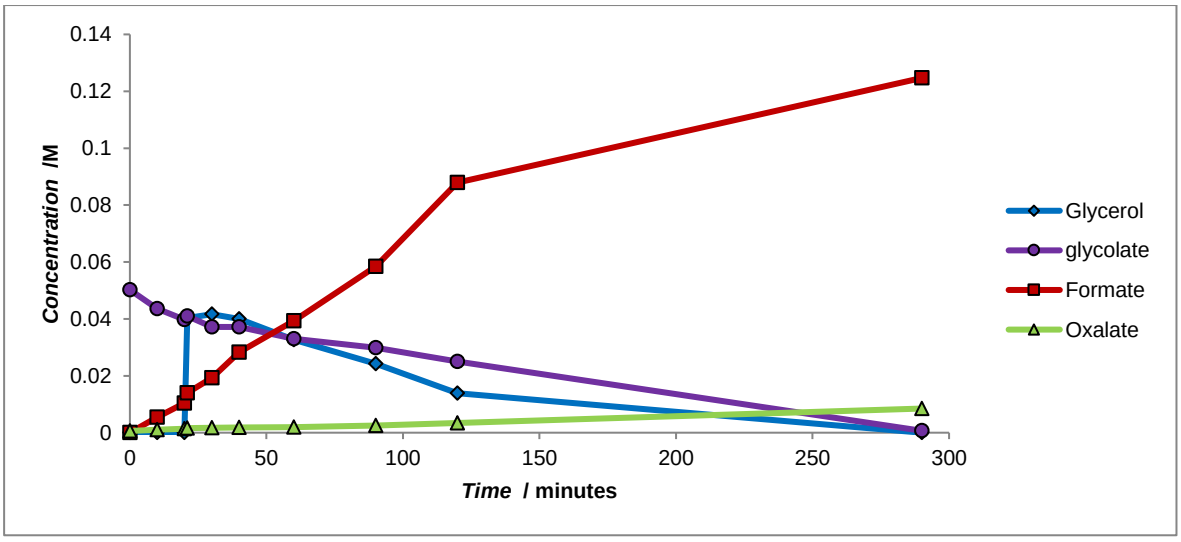
SI 5. Concentration profile of formate and glycerol in competition experiment. In this experiment the catalytic selectivity in the presence of both formate and glycerol is studied. Formate concentration increases when glycerol is present and reduces after glycerol is depleted. This suggests preferential oxidation of glycerol over formate.



SI 6. Concentration profile for the oxidation of oxalate in 1 M KOH at 100 mA/cm^2 on Ni_3S_2/NF.



SI 7. Concentration profile of glycolate, formate and oxalate during electrolysis of glycolate on Ni_3S_2/NF anode at 100 mA/cm^2.



SI 8. Competition experiment to study relative oxidation rates of glycerol and glycolate.

Effect	Model coefficient estimate	Lower 95%	Upper 95%
[glycerol]	-33.55	-43.02	-24.09
excess substrate feed	0.12	0.037	0.21
[glycerol]*excess substrate feed	0.16	-0.021	0.34
Excess substrate feed * excess substrate feed	-0.0027	-0.0058	0.00034

SI 9: The coefficient of each effect in the model obtained from the DoE and the confidence interval ($\alpha = 0.05$)

```
Fit Model(
    Y( :Faraday yield ),
    Effects(
        :"[Glycerol]"n, :Excess substrate feed,
        :"[Glycerol]"n * :Excess substrate feed, :Theoretical conversion 2,
        :Excess substrate feed * :Theoretical conversion 2,
        :Excess substrate feed * :Excess substrate feed
    ),
    Personality( "Standard Least Squares" ),
    History(
        Effects(
            :"[Glycerol]"n, :Excess substrate feed,
            :"[Glycerol]"n * :Excess substrate feed, :Theoretical conversion 2,
            :"[Glycerol]"n * :Theoretical conversion 2,
            :Excess substrate feed * :Theoretical conversion 2,
            :"[Glycerol]"n * :Excess substrate feed * :Theoretical conversion 2,
            :Excess substrate feed * :Excess substrate feed
        )
    ),
    Emphasis( "Effect Screening" ),
    Run(
        Profiler(
            1,
            Confidence Intervals( 1 ),
            Term Value(
                "[Glycerol]"n( 0.525, Lock( 0 ), Show( 1 ) ),
                Excess substrate feed( 66.61, Lock( 0 ), Show( 1 ) ),
                Theoretical conversion 2( 68.357, Lock( 0 ), Show( 1 ) )
            )
        ),
        :Faraday yield << {Summary of Fit( 0 ), Analysis of Variance( 0 ),
        Parameter Estimates( 1 ), Effect Details( 0 ), Lack of Fit( 0 ),
        Sorted Estimates( 0 ), Plot Actual by Predicted( 1 ), Plot Regression( 0 ),
        Plot Residual by Predicted( 1 ), Plot Studentized Residuals( 1 ),
        Plot Effect Leverage( 0 ), Plot Residual by Normal Quantiles( 0 ),
        Box Cox Y Transformation( 0 )}
    )
)
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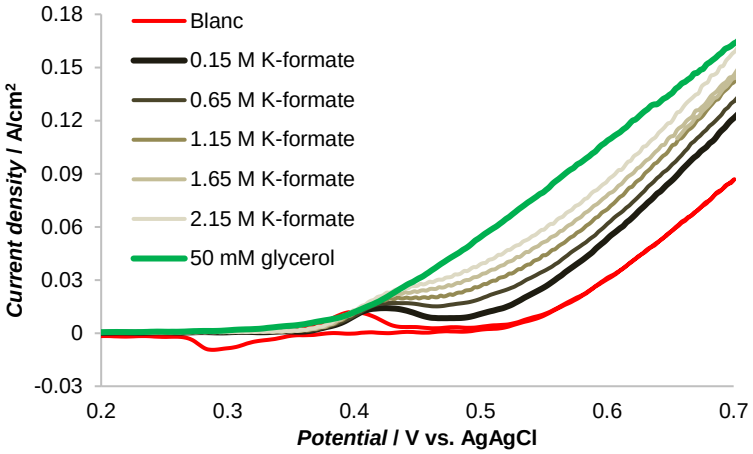
SI 10: Script used for making the model from the data using JMP 16

$$FE\ to\ formate = 72.94 - 33.56 * [glycerol] + 0.12 * excess\ feed + 0.16 * (excess\ feed - 66.61) * ([glycerol] - 0.525) - 0.0027 * (excess\ feed - 66.61) * (excess\ feed - 66.61)$$

SI 11. Model for the FE to formate resulting from the DoE.



SI 12. CV of Ni_3S_2 in 1 M KOH (red line), LSV for various concentrations of formate and 50 mM glycerol. Scan speed = 5 mV/s