Clean Hydrogen Partnership

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EXSOLUTION-BASED NANOPARTICLES FOR LOWEST COST GREEN HYDROGEN VIA ELECTROLYSIS

EXSOTHyC

CCD approach for Zirfon material with optimal binder/catalyst choice, serving as benchmark CCD

(Deliverable D3.1)

The project is supported by the Clean Hydrogen Partnership and its members		
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NOTICES

For information, please contact the project coordinator, Elo Meier, e-mail: elo.meier@stargatehydrogen.com. This document is intended to fulfil the contractual obligations of the EXSOTHyC project, which has received funding from the Clean Hydrogen Partnership and its members, concerning deliverable D3.1 described in contract 101137604.

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Reviewer(s)

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Table of revisions

Version	Date	Description and reason	Author	Affected sections
v1.0	15.01.2025	First draft ready to be reviewed	Maximilian Demnitz	All
V2.0	17.01.2025	Draft technical description confirmed. Some changes made in the structure and template of the deliverable.	Raymond Thür, Stefan Loos, Elo Meier	All
V3.0	20.01.2025	Final version is ready	Maximilian Demnitz	All

List of Partners

Stargate Hydrogen Solutions OÜ (Stargate)
University of St Andrews (St Andrews)
Agfa-Gevaert NV (AGFA)
Eindhoven University of Technology (TUE)
Fraunhofer IFAM (IFAM)

List of Abbreviations

AEM – anion exchange membrane
HER – hydrogen evolution reaction
HOR – hydrogen oxidation reaction
HTO – hydrogen to oxygen crossover
ISM – ion solvating membrane
OER – oxygen evolution reaction
ORR – oxygen reduction reaction
OTH – oxygen to hydrogen crossover
PGM – Platinum Group Metals
Ra-Ni – Raney-Nickel
RC – recombination catalyst

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1 Objectives

The D3.1 is part of the development of catalyst coated diaphragms do be used in electrolysers and the aim of D3.1 is to showcase the work that has been done between M1-M12 in T3.1 of WP3 “Catalyst coated membrane development”.

The goal was to develop catalyst coated diaphragms (CCDs) that can sufficiently reduce the cell potential and serve as a benchmark for future catalyst coated diaphragms with novel exsolution catalysts.

2 Methodology and Work done

This task was approached by a two-fold idea:

1. Developing a CCD that specifically targets the hydrogen evolution reaction (HER) using conventional catalysts
2. If the first point is proven to be successful, the CCD principle will be applied to both the HER and the oxygen evolution reaction (OER) simultaneously.

The work carried out under both ideas is further described below.

2.1 CCD development for HER

For the enhancement of the HER three prominent catalysts that are commonly employed for water electrolysis were chosen: 20 wt.% Pt/C (20% platinum on 80% graphitized carbon support), nanoparticulate Pt (>200 nm), and Raney Ni (porous Ni). Pt is often used as a reference catalyst usually viewed as being the best performing HER catalyst, even under HER conditions. Raney Ni is a typical high surface area HER catalyst employed for alkaline water electrolysis. As a binder PVA was chosen as it is a cheap polymer which is widely available and biodegradable. A slurry was made from solvent, PVA, and catalytic particles, which was then either sprayed or stencil coated onto the Zirfon UTP 500 diaphragm. The electrical contact between the current deliverer and collector is ensured via Ni porous transport layers (PTL), see Figure 1.

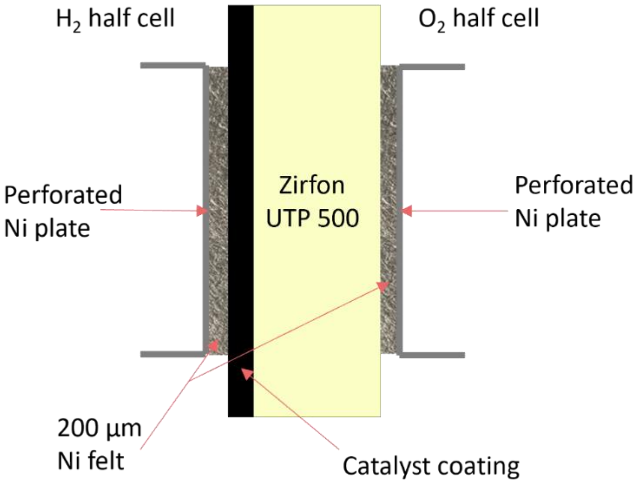

Figure 1. Schematic representation of the CCD, PTL, electrode assembly within the flow cell.

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At high current densities we see a reduction in the cell potential by 200 mV using Raney Ni and 100 mV using Pt based catalysts (see Figure 2). This reduction was achieved by only improving the HER. Interestingly, we observed that the Pt performed decently at low current densities, however, not well at high current densities. In comparison Raney Ni performed great throughout the entire current density range.

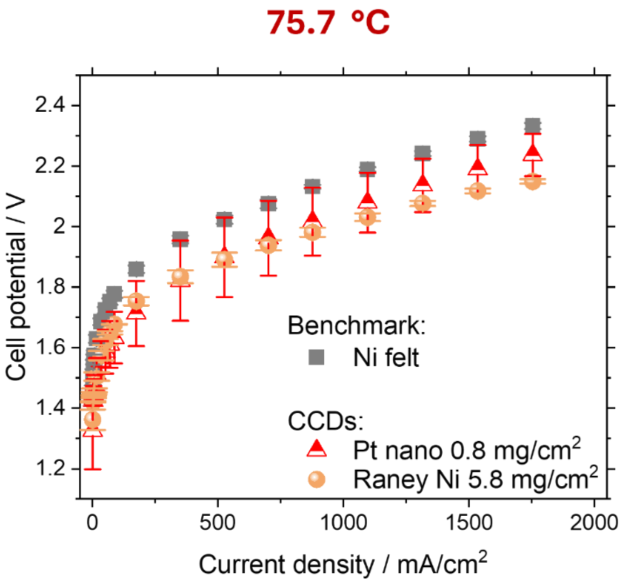

Figure 2. Comparison of cell potential curves recorded for benchmark with Ni felt and Zirfon UTP 500, a CCD made with nanoparticular Pt and a CCD made with Raney Ni in 27 wt.% KOH at around 75 °C. For the anode a Ni felt was used as well.

This trend could be well observed in the internal resistance corrected polarization curves, which showed a change in Tafel slope between low and high current densities for Pt based catalysts at around 30 mA/cm^2. This trend was observed through multiple truly independent samples as well as at different temperatures (see Figure 3).

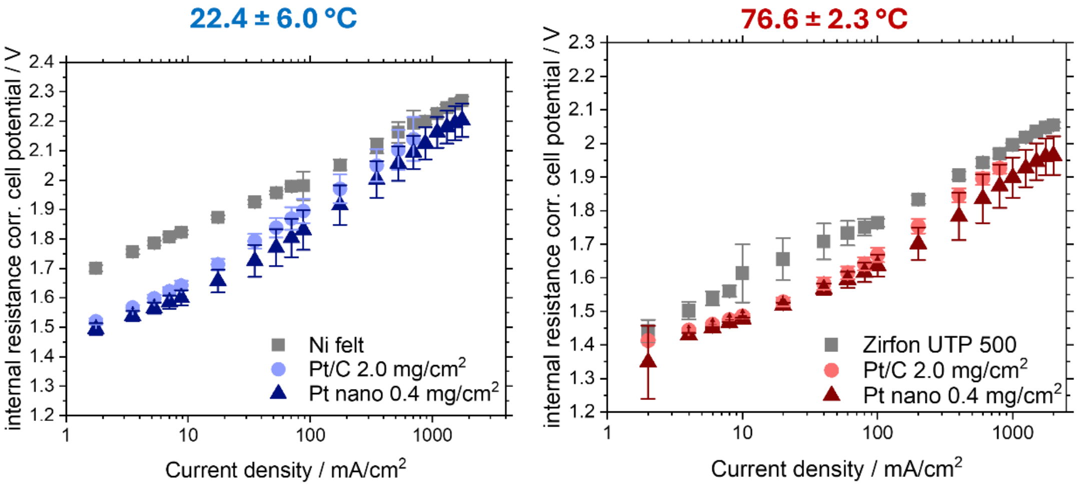

Figure 3. Polarization curves showcasing the total internal resistance corrected cell potential of benchmark Ni felt and Zirfon UTP 500 and CCDs coated with either Pt/C or nanoparticular Pt applied for the HER in 27 wt.% KOH with 50 μM Fe.

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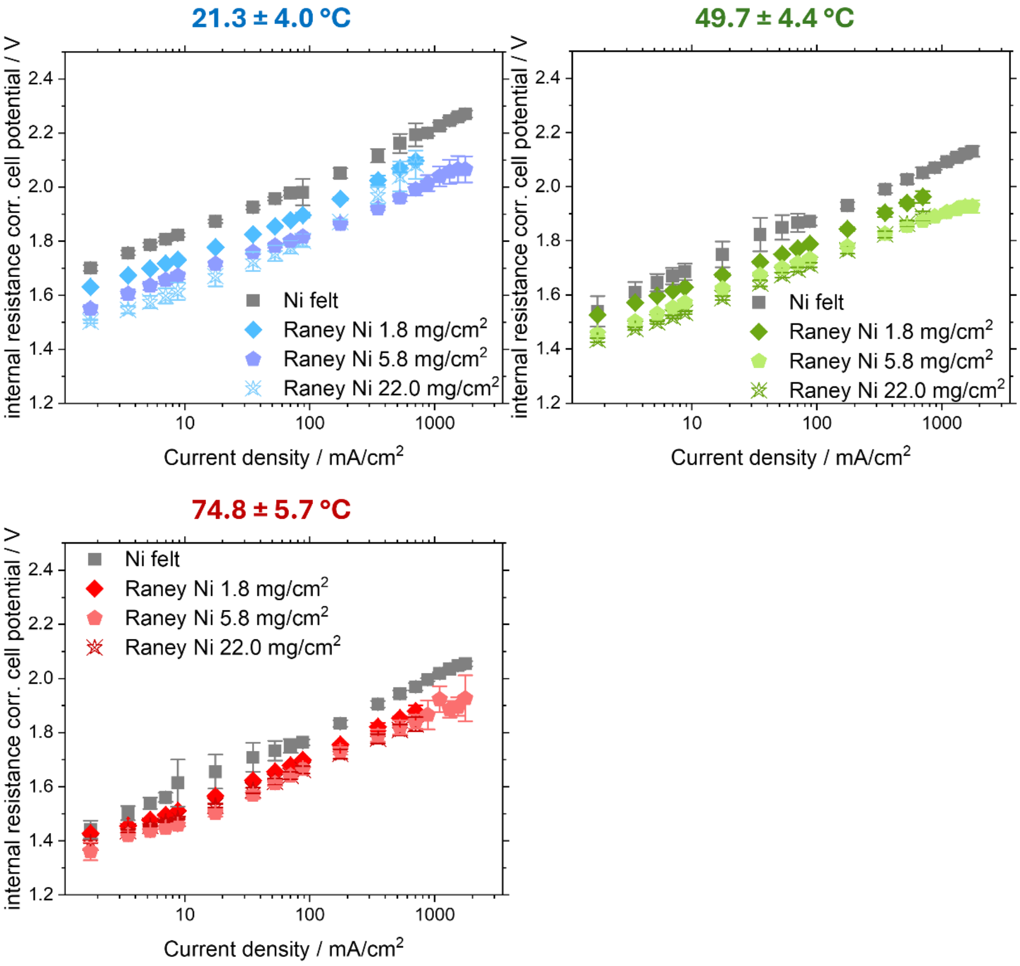


Figure 4. Polarization curves showcasing the total internal resistance corrected cell potential of benchmark Ni felt and Zirfon UTP 500 and CCDs coated with varying loadings of Raney Ni applied for the HER in 27 wt.% KOH with 50 µM Fe.

In contrast, such a trend could not be observed for CCDs prepared with Raney Ni, which showed a consistent decrease in potential with increasing Raney Ni catalyst loading (see Figure 4). In our view this is connected to the decrease in capacitance for Pt with increasing current density, which was not observed for Ni (see Figure 5). We can speculate that in alkaline conditions the H-Pt binding energy is higher than under acidic conditions. This procedurally leads to the saturation of Pt surface sites with H, which will not form H_2 due to the high binding energies.

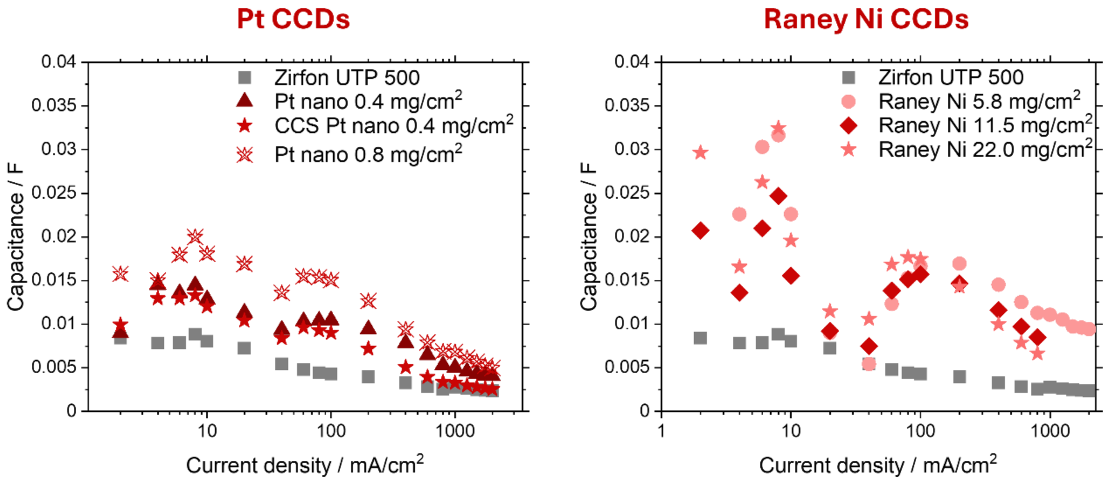


Figure 5. Capacitances for Pt CCDs determined via the Brug equation **Error! Reference source not found.** of benchmark Ni felt and Zirfon UTP 500 and CCDs coated with nanoparticular Pt or Raney Ni applied for the HER in 27 wt.% KOH with 50 µM Fe.

Long-term tests were performed over the course of 60 h, where we observed that the CCDs were not stable over long periods of time. This is connected to the PVA dissolving over time at high temperatures into the electrolyte. Especially, the Pt based CCDs showed a fast delamination, while Raney Ni CCDs reached a stable equilibrium after some hours (see Figure 6). The delamination occurred from the Zirfon diaphragm towards the PTL, which was observed optically and in SEM (see Figure 7 and Figure 8). The delamination was observed for both Raney Ni and Pt based CCDs, however, Pt/C showed a higher resistance towards delamination than purely metal based catalysts.

While the stability was not optimized yet, due to time constraints, we sought to apply the CCD concept to both HER and OER, to see what kind of electrochemical performances were possible.

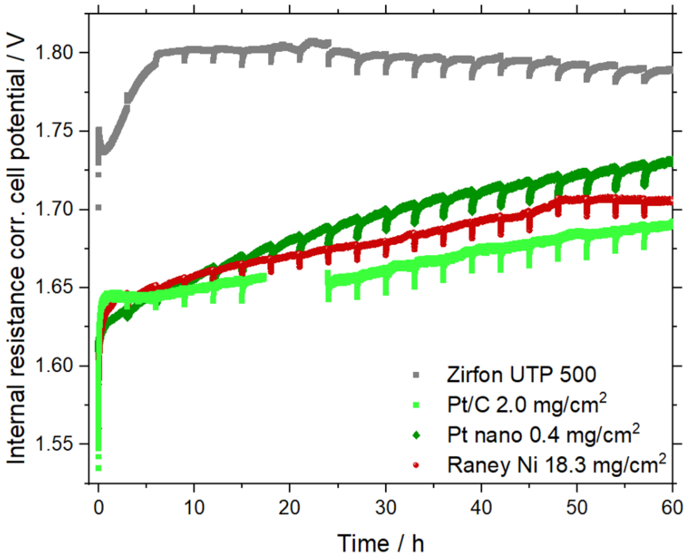


Figure 6. Stability chronopotentiometry measurement at ~90 mA/cm^2 of a Ni felt and Zirfon UTP 500, a CCD made from Pt/C with PVA on Zirfon UTP 500 (2.0 mg/cm^2), a CCD made from nanoparticular Pt with PVA on Zirfon UTP 500 (0.4 mg/cm^2) and a CCD made from Raney Ni with PVA on Zirfon UTP 500 (18.3 mg/cm^2) up to 85 h in 27 wt.% KOH with 50 µM Fe at 85 °C.

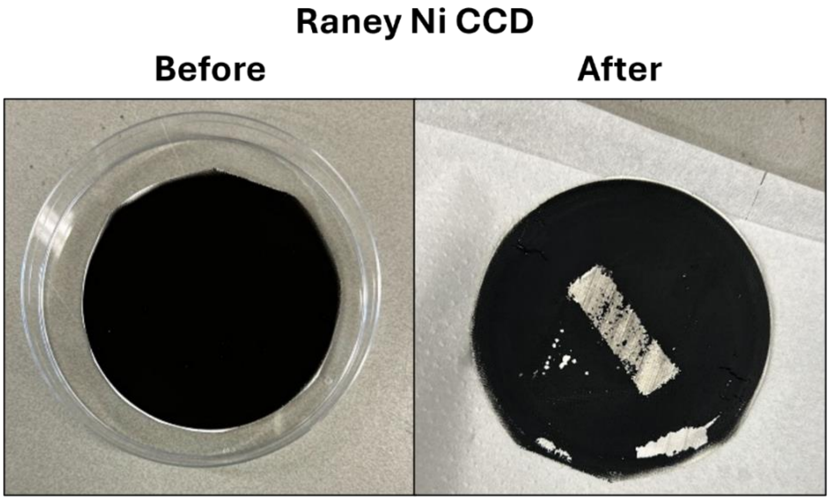


Figure 7. Optical image of a 11.5 mg/cm^2 Raney Ni CCD pre- and post-electrolysis. The Raney Ni in the contact area (white) was delaminated onto the PTL after disassembly of the cell post electrolysis.

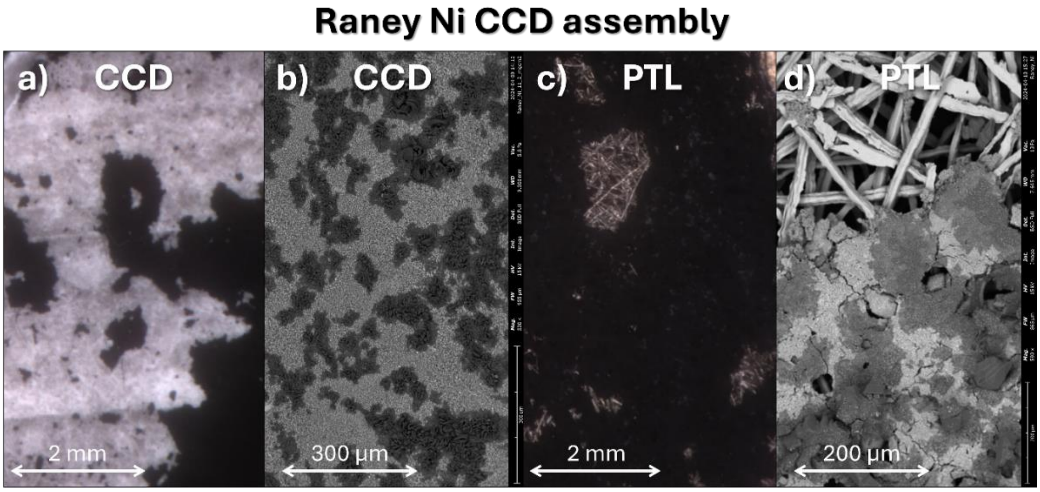


Figure 8. a) Optical image and b) SEM image of a Raney Ni CCD (11.2 mg/cm^2) post electrolysis as well as c) optical image and d) SEM image of the PTL post electrolysis used in the same experiment on the cathodic side.

2.2 CCD development for HER and OER

As the CCDs for HER showed good performance, we coated Zirfon UTP 500 and 220 on both sides to obtain double coated CCDs. For the HER CCD Raney Ni was used as it showed the best performance in our previous experiment and for the OER we used FeNi LDH, which is regarded as one of the best and cheapest OER catalysts. As a coating procedure we applied spray and stencil coating, with a stronger focus on stencil coating, as it is quicker and easier to scale to larger sizes than spray coating.

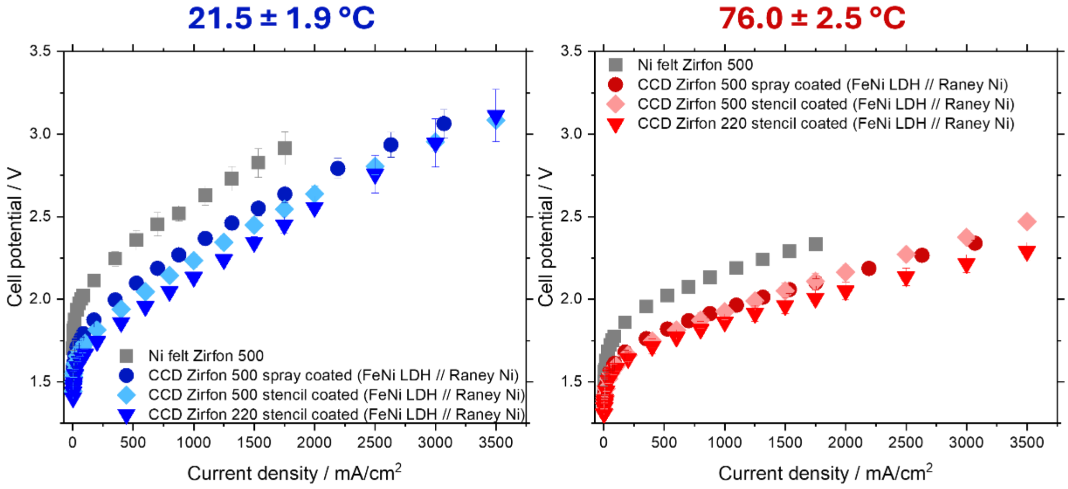


Figure 9. Polarization curves obtained for benchmark Ni felts and Zirfon UTP 500, compared to catalyst coated diaphragms (Zirfon UTP 220 and 500) at varying temperatures in 30 wt.% KOH. 50 µM Fe concentration was used in the stencil coated CCD experiments, while a 500 µM Fe concentration was used for the spray coated CCD.

Using this approach, we achieved at 21.5 °C for Zirfon UTP 500 a reduction of 300 mV and at 76.0 °C a reduction of 230 mV against the reference without CCDs. We additionally performed experiments with double coated on Zirfon UTP 220, which resulted in a total reduction of 400 mV and 330 mV at 21.5 and 76.0 °C, respectively, due to an additional reduction in ohmic resistance. Both spray and stencil coated CCDs showed similar performance and reduced the cell potential sufficiently to allow for great performances even at current densities far above 1 A/cm^2. The CCDs also did not lead to an increase in ohmic resistance (see Figure *10*).

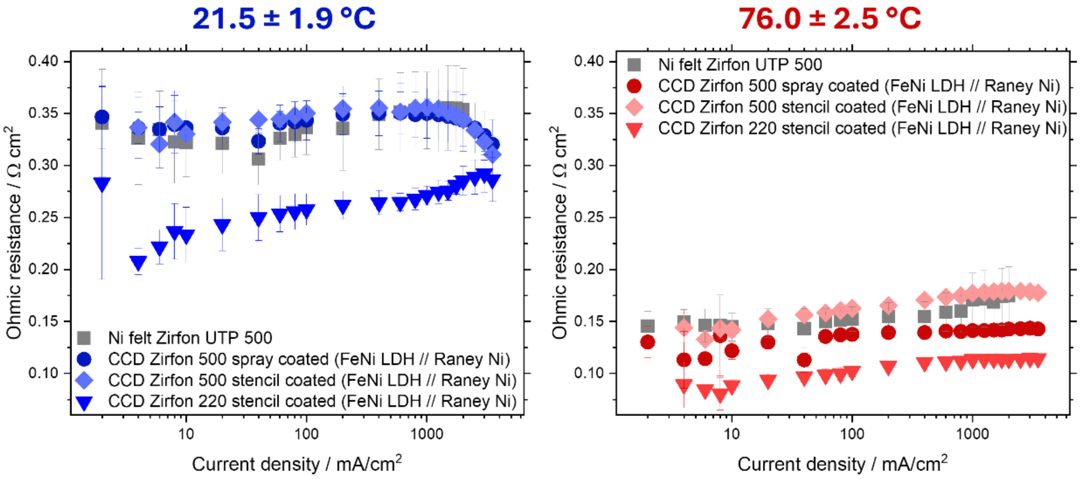
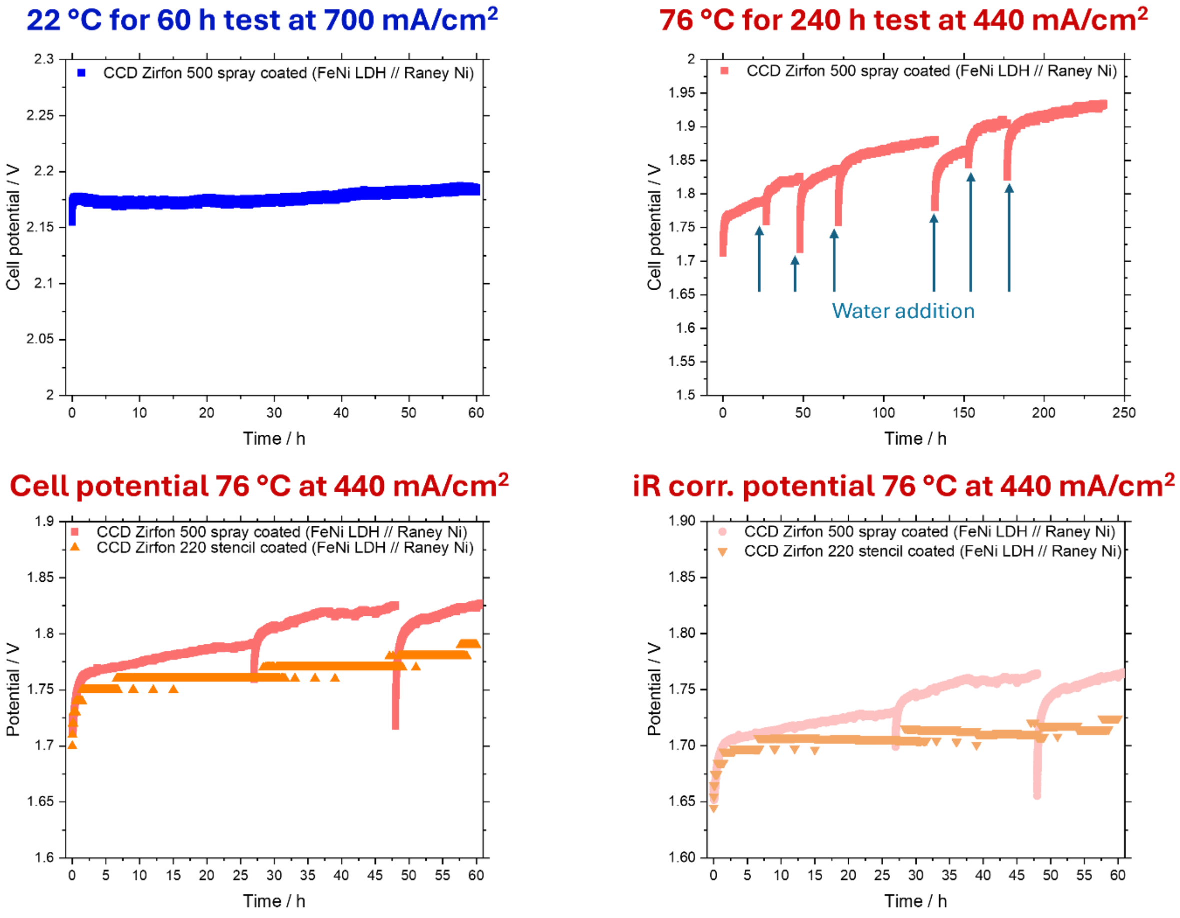


Figure 10. Ohmic area resistances obtained for benchmark Ni felts and Zirfon UTP 500, compared to catalyst coated diaphragms (Zirfon UTP 220 and 500) at varying temperatures in 30 wt.% KOH. 50 µM Fe concentration was used in the stencil coated CCD experiments, while a 500 µM Fe concentration was used for the spray coated CCD.

For the double coated CCDs long-term testing was performed as well (see Figure 11). At 22 °C no degradation can be observed. However, at 76 °C we observed degradation for the spray coated CCD, however, not for the stencil coated CCD. As with the previous study, PVA has proven to be not the most stable binder material as it dissolves over time. However, other promising binder polymers are being investigated as part of the EXSOTHyC project, which can very well prove to be more stable and allow for long-term operation of CCDs.

With these studies we also want to highlight that we were able to reduce the cell potential by at least 300 mV, as was promised in the work package goals.



22 °C for 60 h test at 700 mA/cm²

76 °C for 240 h test at 440 mA/cm²

Cell potential 76 °C at 440 mA/cm²

iR corr. potential 76 °C at 440 mA/cm²

Figure 11. Long-term stability test of the spray and stencil coated CCDs (FeNi LDH // Raney Ni) at 20°C at 700 mA/cm^2 and at 85 °C at 440 mA/cm^2 in 30 wt.% KOH. 50 μM Fe concentration was used in the stencil coated CCD experiments, while a 500 μM Fe concentration was used for the spray coated CCD.

3 Deviations

There are no significant deviations from the initial workplan and all the expected result have bene achieved.

4 Conclusions

Within this work package we successfully made CCDs, which showed great performances, especially at high current densities, which are currently not reached in alkaline water electrolysis. This shows that high current densities are indeed achievable using alkaline water electrolysis, if ohmic and polarization resistances in the cell are addressed accordingly. We could also show that simple catalyst, such as Raney Ni or FeNi layered double hydroxides that are easy to purchase or synthesize, still show great promise for the field of alkaline water electrolysis.

Platinum on the other hand has been seen to not work optimally under alkaline conditions, showing an improvement around the same as Raney Ni at low current densities and a deactivation of the catalyst at higher current densities. As such it can be doubted if the rare and expensive metal is suitable for alkaline water electrolysis in general.

Lastly, the stability of CCDs for long-term applications needs to be improved with a suitable polymer binder that can withstand conditions in an electrolyser at currents of > 1 A/cm^2 and 85 °C in 30 wt.% KOH. We expect that such a binder will be found within the project, however, the performance with such a binder might not be as great as with PVA. Nevertheless, this is necessary as industry demands on catalysts are naturally based on long-term operations over thousands of hours.

Both studies were also published open access and are available for more detailed information.

- https://doi.org/10.1016/j.ijhydene.2024.10.048
- https://doi.org/10.1149/1945-7111/ada581