Deliverable Report

Report on Milestone MS6 "Current density @0.75 A/cm^2 with eta=80% on HHV basis demonstrated with 300 cm^2 electrodes" and specification of the electrodes (D4.2)

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Revisions

Version	Changes
2	Non-public information eliminated

Contents

Abbreviations and Indices

Abbreviation	**Explanation**
RES	Renewable energy systems
RHE	Reversible hydrogen electrode
DOW	Description of Work
VPS	Vacuum plasma spraying
RHE	Reversible hydrogen electrode
XRD	X-ray diffraction
OCV	Open cell voltage

0. Summary

The aim of this document is to present the close approach to deliverable D4.2 “Report on Milestone MS6 <<Current density @0.75 A/cm^2 with eta=80% on HHV basis demonstrated with 300 cm^2 electrodes>>”.
Electrodes were developed and many coating process parameters varied for a 4 cm^2 half cell test at ambient pressure. For electrodes performing well 300 cm^2 electrodes were coated and tests with these performed in single cells of conventional design or with e-bypass separator.
The best achieved efficiency in single cell at 300 cm^2 at 750 mA/cm^2 was an efficiency of 76% on HHV basis at 80°C. For a smaller cell in tests with electrodes coated with almost the same VPS parameters (coating and test of these electrodes was not part of the project) an efficiency above 80% was achieved at FZ Juelich with conventional separators.

1. Introduction

Electrodes for alkaline electrolysers should be low-prized, highly efficient, long-term stable also in intermittent operation of the electrolyser and easy to produce in an industrial manner. Today electrolysers are usually equipped with nickel foil- or wire based electrodes or steel electrodes coated galvanically with nickel. To increase stability and efficiency the cathode (hydrogen evolution electrode) is additionally coated by noble metals. However this increases the costs.

DLR has developed a coating for alkaline electrolyser electrodes that does not use noble metals, i.e. the material costs are lower. Porous coatings of Raney-Nickel (NiAl) and NiAlMo-alloy are applied on metal support by vacuum plasma spraying. In an activation step the Al is removed and the coating shows a high nickel surface. The addition of Mo to the cathode increases the stability of the electrode while the electrolyser is switched off and the potentials are not stabilised. During the project coating parameters were varied such that it was adapted to the electrode support suggested by Hydrogenics – nickel expanded metal sheet of 0.5 mm thickness – and that good efficiency and stability could be achieved. This development of coating parameters was done with 4 cm^2 electrodes and the tests performed in half cells at ambient pressure.

Electrodes performing well in half cell tests were also produced in 300 cm^2 size to be tested in a full electrolyser cell. Both a conventional cell design with single commercial separator (Zirfon Perl® by Agfa) and the project cell design with e-bypass membrane were used.

2. Links of this Deliverable in the Project

This deliverable is an output of task 4.3 – “Test of current density/voltage characteristics and long-term performance of the electrodes in laboratory system”. Basis for this deliverable was a selection of electrode materials (Task 4.1) as well as the development and parameter adaptation of Vacuum Plasma Spraying for being able to spray adequate electrodes of technical size with good performance (Task 4.2).

3. Report Results and Achievements

Electrode half cell tests

To develop high efficiency electrodes it was not possible to characterize all electrodes in a 300 cm^2 full cell. Thus the electrode coating parameter variation tests were performed with electrodes of 4 cm^2 size in a half cell setup.

A fair number of electrodes was coated and either the optical aspect of the coating layer was investigated via the microscope image of a cross section or it was tested electrochemically in half cell tests. Appendix A lists the results of electrode coatings.
Half cell tests were performed in a setup described in the RESelyser midterm report figure 1.3.4.7. Usually the KOH concentration was 30 wt%, the normal temperature was 70°C and the tests were run at ambient pressure. The reference electrode was originally a Hg/HgO electrode filled with the same 30 wt% KOH as the test vessel. However, the long-term stability and thus reliability of this electrode turned out to be insufficient. In further tests a Reversible Hydrogen Electrode RHE (Gaskatel) was used. For comparison of the electrode performance typically the voltage at 0.5 A/cm^2 was used. As the reference electrode could not be mounted directly at the electrode surface there is a voltage drop between the electrode and the position where the reference electrode is connected. To correct for this voltage drop and possible contact resistances of the test setup varying from test to test, the IR-corrected voltage was used, i.e. the high frequency impedance (R) between working electrode and reference electrode was measured and as this can be attributed to the ohmic resistance the product of this resistance and the current I was used to correct the voltage. Figure 1 gives a statistics of the IR-corrected voltages at 0.5 A/cm^2 of all electrodes tested with RHE reference electrode on the first day of electrode operation.

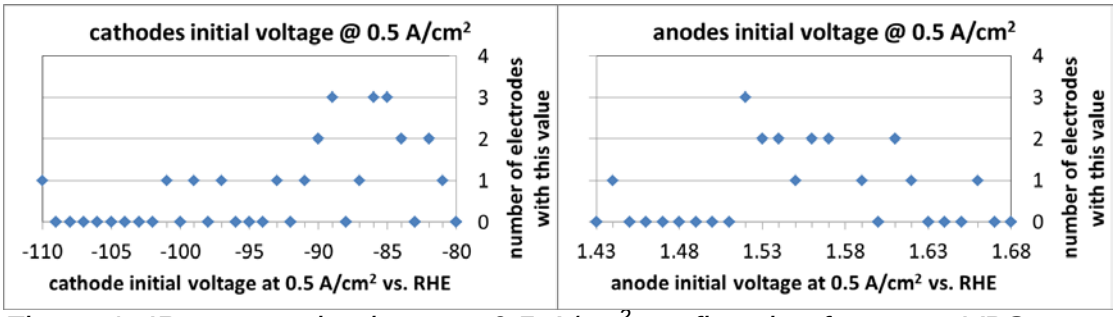


Figure 1: IR-corrected voltage at 0.5 A/cm^2 on first day for many VPS-covered electrodes

It can be seen that most of the cathodes are in a very narrow voltage region between -95 and -81 mV. This range is similar to the measurement and reproducibility error so that in fact all these electrodes show the same initial value. Still coating parameters of the cathodes were varied because for the first generation electrodes an insufficient long-term stability was observed.

For the anode the range of voltages is larger with most electrodes being between 1.520 V and 1.620 V vs. RHE, i.e. within an interval of 100 mV. Also here the first generation electrode's long-term stability was insufficient making parameter variations necessary.

Electrodes with 4 cm^2 area prepared with the same coating parameters as the full cell electrodes described in this report were also characterised in half cell setup.

Figure 2 shows the current voltage curves on the first day of operation of this cathode as well as the results of several days of testing it, all at 70°C in 30 wt% KOH at ambient pressure. The overpotential given in the curves is calculated from the IR corrected electrode potential vs. RHE assuming 0 V overpotential at 0 V vs. RHE. The first day voltage at 0.5 A was -86 V which is quite in the range of all good electrodes coated. Very long-term stability tests of this electrode are not available. It was tested only for 11 days during which it showed constant performance. The coating parameters of this electrode were selected for the large single cell electrode because microscopy images of the cross sections of electrodes with similar parameters showed less porosity than previous electrodes and a better melting and cohesion of the coating layer particles. It was therefore assumed that the stability of the electrodes should be better, especially no detaching of the coating layers.

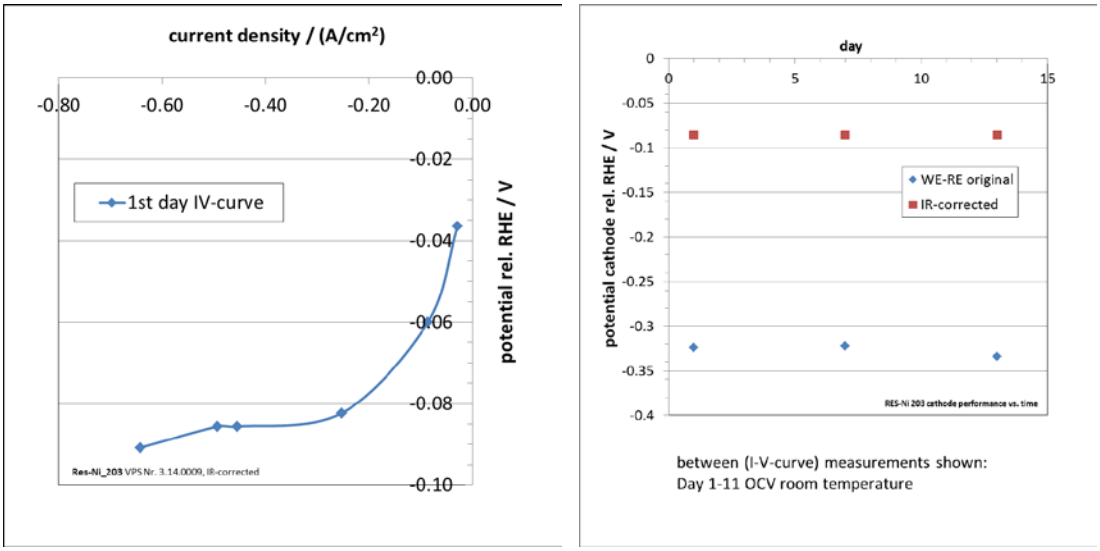


Figure 2: RES-Ni203 cathode with same coating as in single cell. Left: First day iV-curve IR-corrected; right: Short term measurement. Important coating parameters: cathode powder NiAlMo Sulzer, plasma power 28 kW, plasma gas composition Ar:H_2:He 45:6:10, Vacuum pressure: 70 mbar, layers sprayed: 5 with NiAl, 10 with NiAlMo, scan speed: 600 mm/s, heating: 400°C sample RES-EI203.

Figure 3 shows the current voltage curves on the first day of operation of this anode as well as the results of a long-term test on it, all at 70°C in 30 wt% KOH at ambient pressure. The overpotential given in the curves is calculated from the IR corrected electrode potential vs. RHE assuming 0 overpotential at 1.23 V vs. RHE. The first day voltage at 0.5 A/cm^2 of 1.505 V is lower than for most electrodes tested. The long-term behavior shows a gradual increase of the electrode voltage by approximately 100 mV. After 50 days of operation of this electrode much of the coating detached. So this electrode is still not sufficiently stable. Further parameters variation was performed with tests in 4 cm^2 electrodes. However, these improved electrodes could not be tested in the full cell any more.

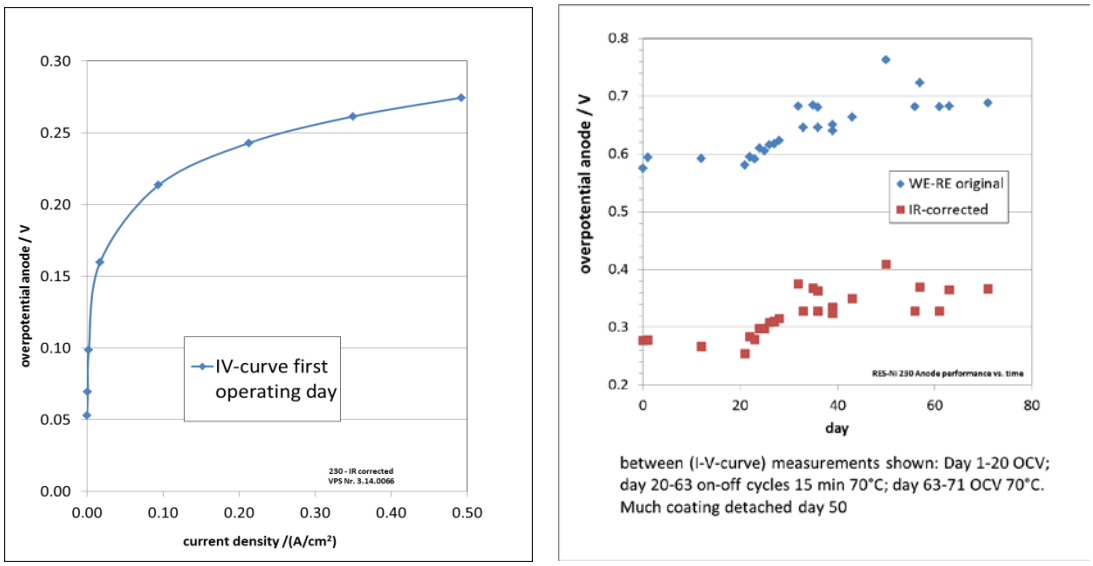


Figure 3: RES-Ni230 same anode coating parameters as for single cell. Left: first day iV- curve IR corrected; right: long-term measurement. Anode Powder NiAl H.C. Starck, plasma power 25 kW, plasma gas composition Ar:H_2:He 45:4:10, Vacuum pressure: ambient pressure, layers sprayed: 14, scan speed: 400 mm/s, heating: 200°C sample RES-Ni230

Electrode coating parameters and materials

The substrate was pre-treated by sand-blasting (to remove the oxide layer and roughen the surface) and subsequently etched in 33% HCl acid. The cathode electrode is coated with an intermediate layer of NiAl (56/44) and an active layer of AlNiMo (44/39/17) (Commercial powders supplied by H.C. Starck). The anode electrode is coated with a layer of NiAl (56/44). The coating thickness is approximately 140 µm for the cathode and approximately 90 µm for the anode. To achieve quite dense layers that have enough mechanical stability high power was supplied to the plasma burner and rather high flows of the gases hydrogen and helium were selected. To avoid too much heating of the substrate the scan speed of the plasma torch over the electrode was selected quite high.

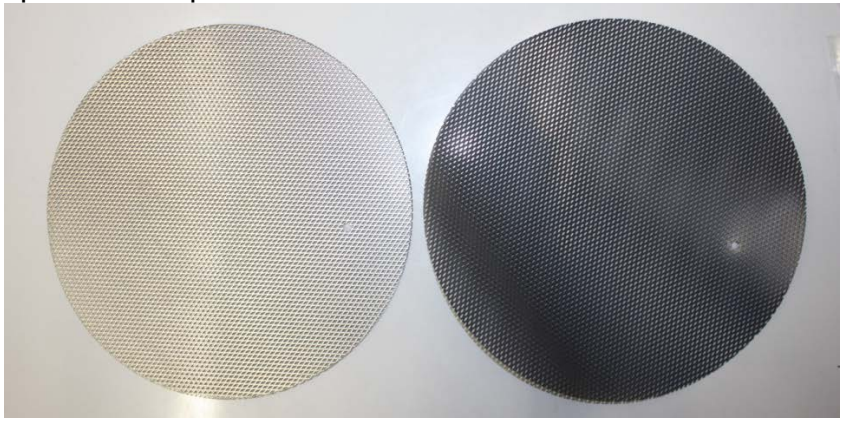


Figure 4: Uncoated electrode (left) and coated electrode (right)

A summary of all the coating parameters during Vacuum Plasma Spraying for the anode is given in this parameter protocol:

Eingabehilfe

VPS DC 3 Produktion

Kunde	RESelyser	**Bearbeiter**	GR	**Datum**	27.01.2013	**Blatt-nummer**	1	**VPS-Nummer**	**3.14.0006**
Projektbeschreibung									
Bemerkung	Heizung 200°C								
Substrat	Ni-Gitter			**Grundplatte**					
Substrathersteller				**Substrathalter**					
Beschichtung	**Elektrolyse**	**Beschicht-ungsfläche**	(cm^2)	**Befestigungs-nummer**					
Programmname									
Brenner-nummer	B 13	**Anoden-nummer**	Mach3/6mm	**Kathoden-nummer**	Medicoat	**Gasverteilerring**	(°)	55	

	Bezeichnung	**Förder-gas**	**Δ-Gewicht** (g)	**Injektions-winkel** (°)	**InjektionsØ** (mm)	**Injektionsabstand axial** (mm)	**Injektionsabstand radial** (mm)
Pulver oben	Ni-Al 56-44 Batch: 30803	Ar			3		
Pulver unten		Ar			3		

		Startwert		**Endwert**	
Anlagen-betriebszeit	(h|m)	16564	48		
Anoden betriebszeit	(h|m)	10	23		
Kathododen-betriebszeit	(h|m)	10	23		
Plasmazeit	(h|m)	156	12		
Anlagen-zündungen		823			
Anoden-zündungen		54			
Kathoden-zündungen		54			
Leistungs-verbrauch	(kWh)	4332.0			
Ar Kessel	(bar)				
Ar Plasma	(bar)				
He Plasma	(bar)				
H_2 Plasma	(bar)				
N_2 Plasma	(bar)				
O_2 Plasma	(bar)				

		Pulver-förderer oben	**Pulver-förderer unten**
Pulverför-dernr.		1	
Rührer	(%)	30	
Gas	(SLPM)	1.8	
Teller-nummer		16x1,2	
Teller-rotation	(U/min)	1.2	
Förder-menge	(g/min)		

Argon	(SLPM)	45
Wasserstoff	(SLPM)	4
Helium	(SLPM)	10
Stickstoff	(SLPM)	
Sauerstoff	(SLPM)	
Kühlwasser-volumenstrom	(SLPM)	13.5
Kühlwasser-leistung	(kW)	10.1

$T_{Heizung}$	(°C)	200
Rampe	(K/min)	---
$T_{Substrat}$	(°C)	---
Regelungsart	(Leist./ Strom)	Leistungsgeregelt
Strom I	(A)	390
Leistung P	(kW)	25
Spannung U	(V)	63
Arbeitsdruck	(mbar)	atm
Abstand	(mm)	80
Lagen		14
Bahnabstand	(mm)	20
Geschwindigkeit	(mm/s)	400
Substratspritz-winkel	(°)	0°
Rotatations-geschwindigkeit	(U/min)	

Substratnummer	**Substrat-verteilung** (z.B.:A1, B2)	**Masse vor Beschichtung** (g)	**Masse nach Beschichtung** (g)	**Δ-Masse** (g)	**Bemerkung Substrat**	
RES-El -62		100.2400	111.8800	11.6400		160µm
RES-El -63		61.7700	71.3500	9.5800	Lochblech	163µm

A summary of all the coating parameters during Vacuum Plasma Spraying for the cathode is given in this parameter protocol:

Kunde	Reselyser	**Bearbeiter**	GR	**Datum**	29.01.2014	**Blatt-nummer**	1	**VPS-Nummer**	**3.14.00010**
Projektbeschreibung	Elektrodenbeschichtung neues NiAlMo-Pulver von Sulzer höhere Leistung								VPS DC 3 Produktion
Bemerkung	Heizung 400°C								
Substrat	Ni-Gitter			**Grundplatte**					
Substrathersteller				**Substrathalter**					
Beschichtung	**Elektrolyse**	**Beschicht-ungsfläche**	(cm^2)	**Befestigungs-nummer**					
Programmname									
Brenner-nummer	B 13	**Anoden-nummer**	Mach3/6mm	**Kathoden-nummer**	Medicoat	**Gasverteilerring**	(°)	55	

Eingabehilfe

	Bezeichnung	**Förder-gas**	**Δ-Gewicht** (g)	**Injektions-winkel** (°)	**InjektionsØ** (mm)	**Injektionsabstand axial** (mm)	**Injektionsabstand radial** (mm)
Pulver oben	NiAl 56/44 Batch: 30803 H.C. Starck	Ar			3		
Pulver unten	Al-Ni-Mo AE10101 Sulzer	Ar			3		

		Startwert		**Endwert**	
Anlagen-betriebszeit	(h|m)	16574	58		
Anoden betriebszeit	(h|m)	11	7		
Kathododen-betriebszeit	(h|m)	11	7		
Plasmazeit	(h|m)	156	56		
Anlagen-zündungen		827			
Anoden-zündungen		58			
Kathoden-zündungen		58			
Leistungs-verbrauch	(kWh)	4349.0			
Ar Kessel	(bar)				
Ar Plasma	(bar)				
He Plasma	(bar)				
H_2 Plasma	(bar)				
N_2 Plasma	(bar)				
O_2 Plasma	(bar)				

		Pulver-förderer oben	**Pulver-förderer unten**
Pulverför-dernr.		1	2
Rührer	(%)	30	30
Gas	(SLPM)	1.0	1.0
Teller-nummer		16x1,2	16x1,2
Teller-rotation	(U/min)	1.2	1.2
Förder-menge	(g/min)		

Argon	(SLPM)	45
Wasserstoff	(SLPM)	6
Helium	(SLPM)	10
Stickstoff	(SLPM)	
Sauerstoff	(SLPM)	
Kühlwasser-volumenstrom	(SLPM)	13.5
Kühlwasser-leistung	(kW)	10.1

$T_{Heizung}$	(°C)	400
Rampe	(K/min)	---
$T_{Substrat}$	(°C)	---
Regelungsart	(Leist./ Strom)	Leistungsgeregelt
Strom I	(A)	460
Leistung P	(kW)	28
Spannung U	(V)	61
Arbeitsdruck	(mbar)	70
Abstand	(mm)	200
Lagen		5 / 10*
Bahnabstand	(mm)	20
Geschwindigkeit	(mm/s)	600
Substratspritz-winkel	(°)	0°
Rotatations-geschwindigkeit	(U/min)	

Substratnummer	**Substrat-verteilung** (z.B.:A1, B2)	**Masse vor Beschichtung** (g)	**Masse nach Beschichtung** (g)	**Δ-Masse** (g)	**Bemerkung Substrat**
Res El 67		101.1200	109.2000	8.0800	5x Pulver1-10x Pulver2 102µm

Table 1: VPS parameters of electrodes (detailed spray protocols): RESel-67 VPS Nr. 3.14.0010 NiAl/NiAlMo Sulzer as cathode; RESel62 VPS Nr. 3.14.0006 NiAl atmospherically sprayed as anode. Important coating parameters: cathode powder NiAlMo Sulzer, plasma power 28 kW, plasma gas composition Ar:H_2:He 45:6:10, Vacuum pressure: 70 mbar, layers sprayed: 5 with NiAl, 10 with NiAlMo, scan speed: 600 mm/s, heating: 400°C sample RES-El67. Anode Powder NiAl H.C. Starck, plasma power 25 kW, plasma gas composition Ar:H_2:He 45:4:10, Vacuum pressure: ambient pressure, layers sprayed: 14, scan speed: 400 mm/s, heating: 200°C sample RES-El62.

After coating of the 300 cm^2 electrodes they all have a bending. If they are not sufficiently flat it will be difficult to incorporate them into an electrolyser cell or stack. The reason for the bending are the heating of the substrate during the deposition, the different thermal expansion coefficients of substrate and coating, tensions in the substrate due to the manufacturing, tensions and bending brought to the electrode during sand-blasting or others. By rolling the bending could be strongly reduced so that all electrodes can now be easily pressed to a flat shape. The bending measured by putting the electrode on the table and measuring the highest elevation is at maximum 7.2 mm for all delivered electrodes (including those for the stack).

Materials used

The **anodes** were coated with a spray-dried NiAl powder by H.C. Starck. The composition is 56 wt% Ni, 44 wt% Al. The maximum of the particle diameter distribution is at 20 µm, with most of the particles being between 6 and 28 µm. SEM images show mostly ball-like powder grains with internal substructure. According to XRD analysis the powder consists of the phase Al_3Ni_2 and some other phases that cannot be clearly identified.

The **cathode** electrodes were coated first with a thin layer of the same NiAl powder that should increase adhesion to the surface because is does not lose so much of its substance during the activation. Afterwards the active layer was sprayed with NiAlMo powder. For the single cell cathode examined in this report the NiAlMo was supplied as an experimental powder by Sulzer-Metco in a smaller batch (6kg). According to Sulzer-Metco the composition is 17 wt% Mo, 37 wt% Ni, 46 wt% Al. The powder particle size distribution is quite narrow: the maximum of the particle distribution is at 24 µm with most of the particles being between 21 and 50 µm. There are few small particles. Powder grains are ball-shaped with internal structure.
Figure 5 displays the XRD spectrum of this powder. The phases $Al_{0.72}\ Mo_{0.225}\ Ni_{0.055}$, $Al_{1.1}\ Ni_{0.9}$ and Al_3Ni_2 are contained in a substantial amount.

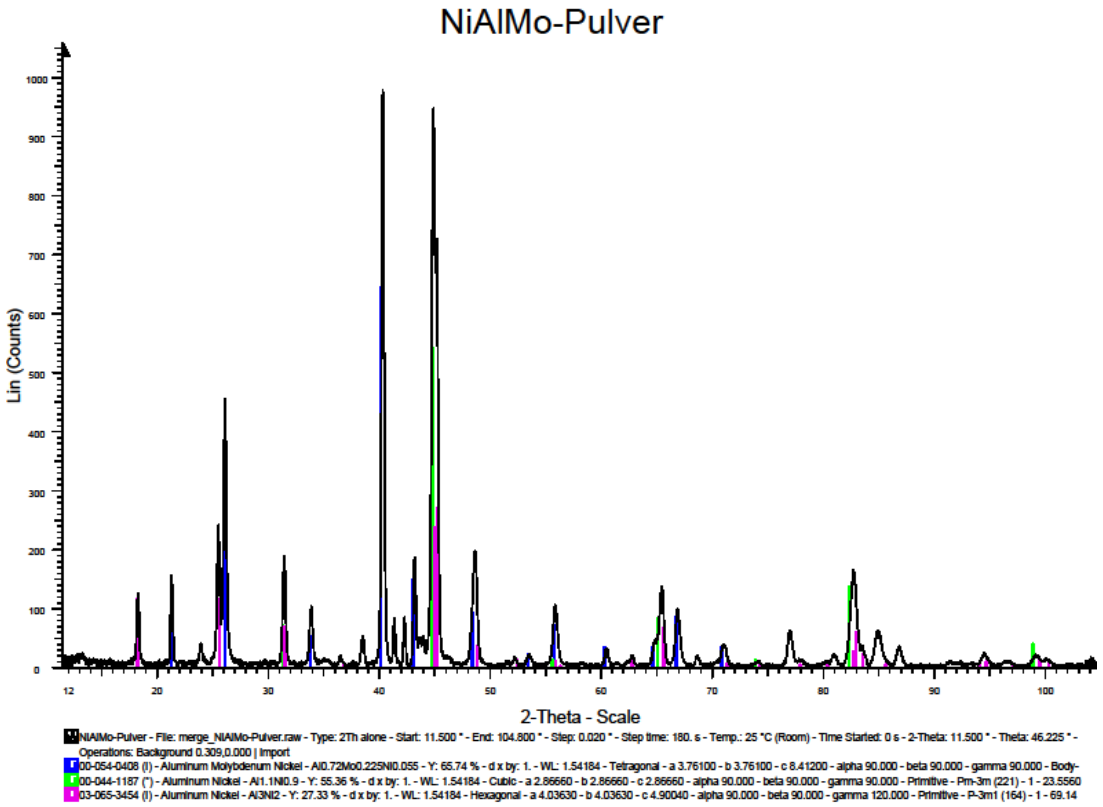


Figure 5: XRD spectrum powder used for the cathode

The **substrate** was a nickel expanded metal sheet supplied by Hydrogenics with thickness of 0.5 mm. The approximately diamond-shaped holes have a length of approx. 2.5 mm and a width of approx. 0.58 mm. The open area of the substrate is approximately 28.6%. The electrode diameter was 206 mm, cut out of a larger sheet probably by waterjet cutting. This gives an electrode area of 333 cm^2.
All current voltage curves for the electrodes are given with respect to the geometrical area of the electrode not considering the holes.

Full cell tests

Cell design

These single cell tests were performed with a cell with e-bypass membrane and compressive seals. The end plates were made of nickel. There were three structure rings made of POM. The cell construction was according to that described in Deliverable D5.1, “concept D” and like the one for the stack described in Deliverable D5.2. However the graphite seals described there were not suitable because they were sealing well but due to their electrical conductivity and the catalytic property of graphite they also acted as electrolyser electrodes. For the single cell measurements the seals were 0.5 mm thick Teflon sheets reinforced at the critical positions by self-adhesive expanded Teflon tape (Flatband 3x1.5 m

by billi Dichtungstechnik GmbH). Figure 6 shows this tape during cell assembly. Figure 7 shows step by step the cell assembly.

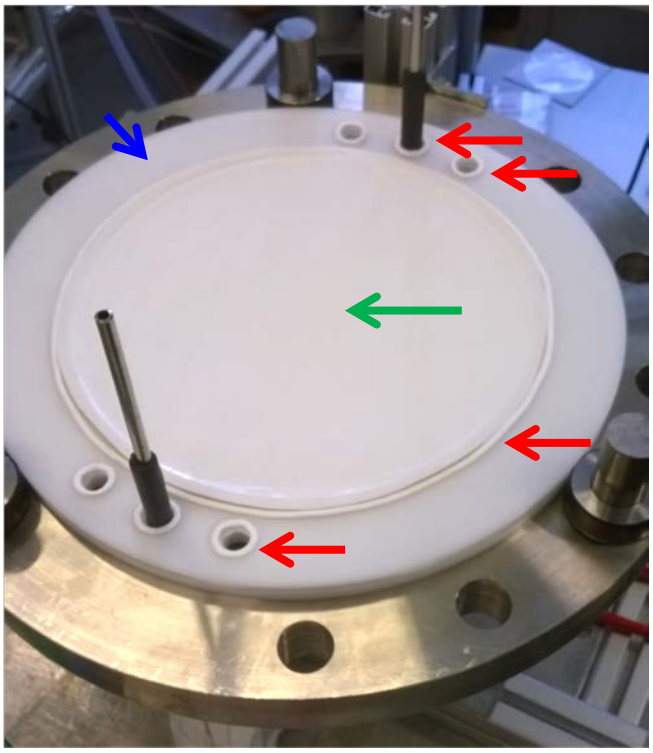
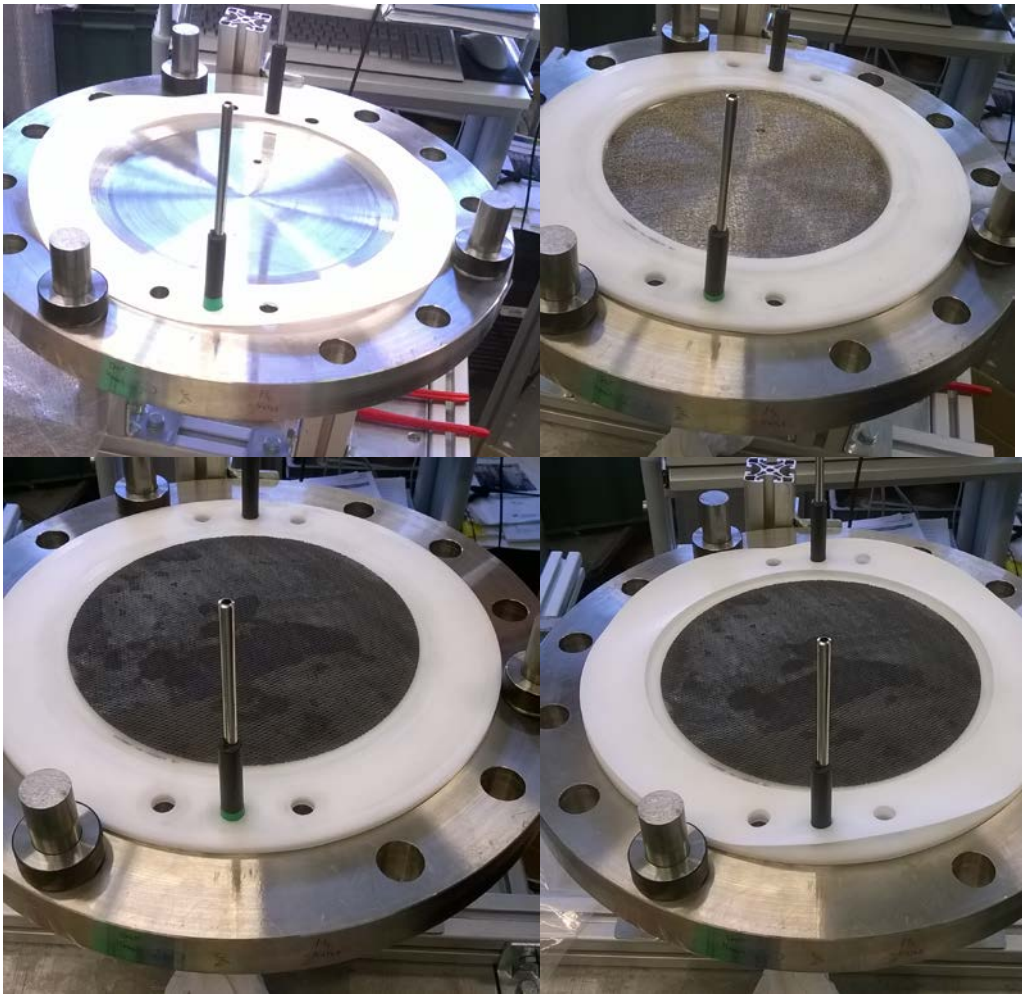
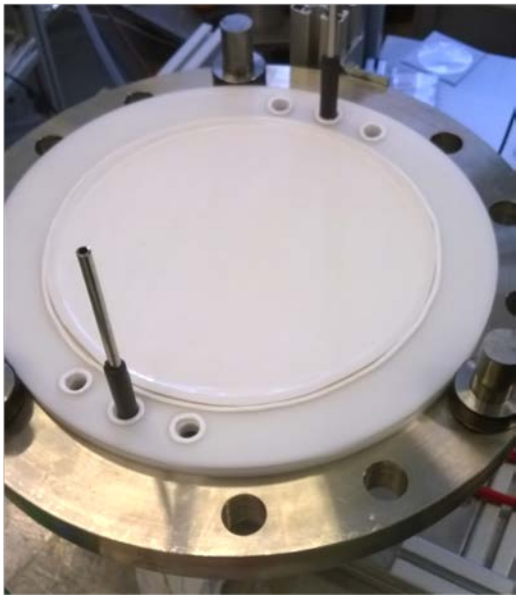


Figure 6: Self-adhesive expanded Teflon seal (red arrows) applied to the middle structure ring to reinforce the sealing at critical positions where height differences in the construction had to be sealed. Green arrow: e-bypass separator; blue arrow: middle structure ring.





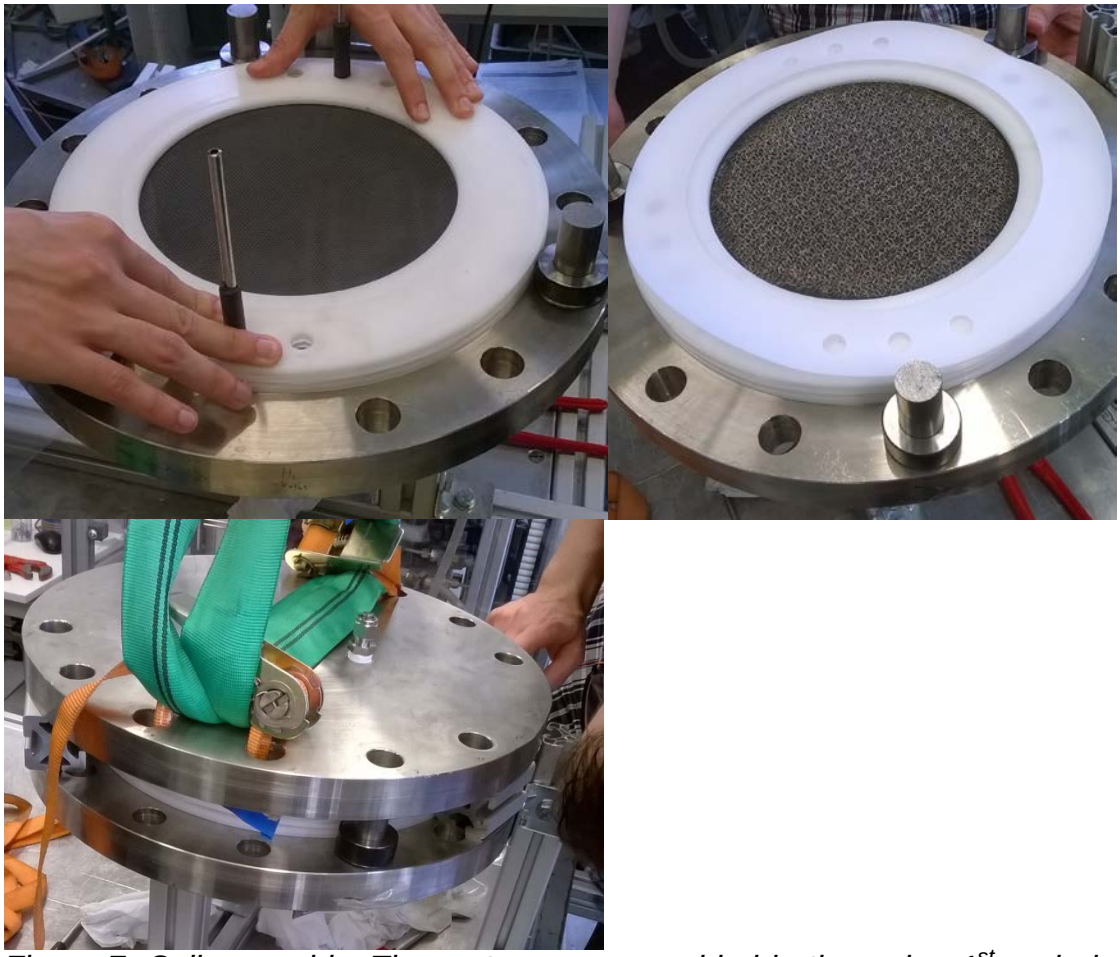


Figure 7: Cell assembly. The parts were assembled in the order: 1st end plate, first teflon seal, first structure ring, first pre-electrode, first electrode, second Teflon seal, middle structure ring assembled with e-bypass separator and self-adhesive Teflon flatband on both sides, third Teflon seal, second electrode, second pre-electrode, second structure ring, fourth Teflon seal turned such that no access of KOH to the end plate was possible in the small holes, second end plate.

The electrodes have their coated faces towards the separator. Even though the electrode geometrical area is 333 cm^2, only 300 cm^2 are assumed to participate in the electrolysis process. The outermost part of the electrode is covered by the structure ring so that it is not electrically contacted, KOH access and gas bubbles evacuation is difficult there. The open area of the structure ring is 300 cm^2 (open diameter 195.4 mm) so that the active electrode area used for calculations is 300 cm^2.

The pre-electrode is a woven structure made of nickel wire. It is quite compressible and has to ensure the electrical contact of the electrode without interfering too much with the gas transport out of the cell. It was supplied by Hydrogenics.

The separators used in this test were e-bypass separators supplied by VITO (first delivered to Hydrogenics, from there to DLR in August 2014). It was a low

permeability separator. After cell assembly the permeability was tested to make sure that there were no leaks. With dest. water at room temperature the permeability from cell middle to anode was 127.7 l/(h m^2 bar), to cathode 123.9 l/(h m^2 bar).

Activation procedure

After assembly of the cell and mounting it in the test station the electrodes were activated in situ. A mixture of 30wt.% KOH solution and 10wt.% K-Na-Tartrate-Tetrahydrate was filled in the gas separators. It had non-pumped access to the cathode and anode compartment of the cell and it was pumped in the middle compartment of the cell to make sure that the electrodes were well wetted and that the evolving hydrogen bubbles are removed from the cell. During activation the cell was heated to 80°C. Activation procedure was run for 24 hours. Then the KOH solution in the test station was replaced by fresh KOH.

Current/voltage curves

The cell was operated with 30 wt% KOH solution at 5 bar absolute pressure. KOH passive flow through the anode and cathode compartment with convective supply of the KOH from the gas separator was possible. In addition KOH was pumped into the middle of the cell forcing it through the separator faces with a flow of 15 ml/min. The differential pressure from middle compartment to anode respectively cathode compartment was 112 mbar. KOH was pre-heated to 50°C and the cell end plates were heated by heat pads to the desired temperature of 80°C measured in the middle of the end plates. Current-voltage curves were measured starting at OCV up to 1 A/cm^2 and back with galvanostatic control, with 7 load points waiting for 4 min at each point. Figure 8 shows the iV-curve at 80°C and as comparison also at 70°C. These curves were measured on the second day of operation of the cell. At 80°C the cell voltage was measured as 1.965 V (interpolated value) at 0.75 A/cm^2 (η=76.5% on HHV basis).

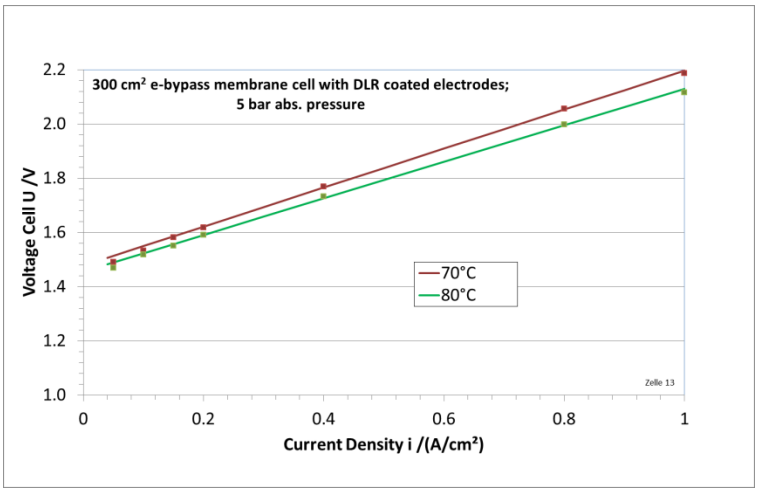


Figure 8: Current voltage curve of a single cell equipped with VPS coated electrodes

Electrodes with the same coating parameters were also coated for FZ Jülich for a test. This coating was not done in the frame of the project but is reported here. The electrodes were activated and assembled in a small electrolyser cell with commercial Zirfon Perl as separator. KOH was pumped through the cell. The current voltage curves obtained with this separator and alkaline membrane separators are not yet published. An efficiency above 80% was achieved [Carmo15]. A new cell setup and suitable operating conditions as well as a shorter distance between the electrodes should make it possible also at 300 cm^2 to achieve these high efficiency values.

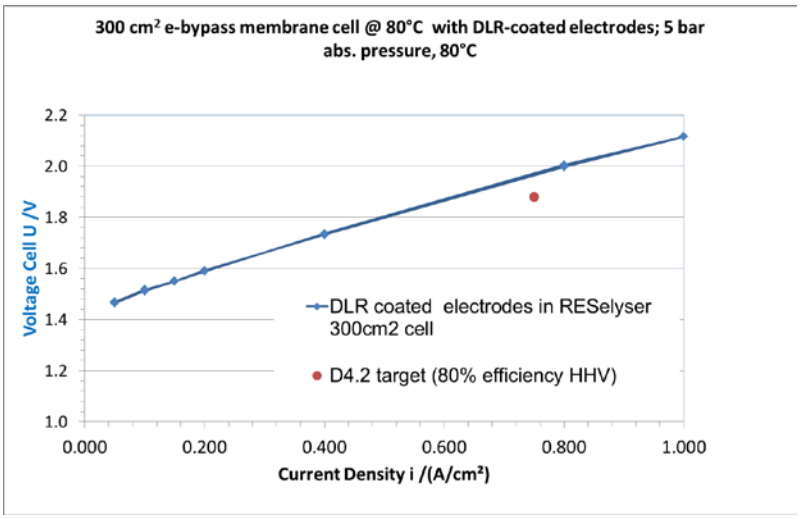


Figure 9: Blue: Current voltage curve of cell with E-bypass separator, VPS coated electrodes, single cell with 300 cm^2 area. Operating parameters: cell temperature 80°C, KOH flow in middle compartment 15 ml/min, 5 bar_{abs}, 30 wt% KOH solution, passive KOH flow in anode and cathode. Important coating parameters for blue curve: cathode powder NiAlMo Sulzer, plasma power 28 kW, plasma gas composition Ar:H_2:He 45:6:10, Vacuum pressure: 70 mbar, layers sprayed: 5 with NiAl, 10 with NiAlMo, scan speed: 600 mm/s, heating: 400°C.$_{sample\ RES\text{-}El67}$*. Anode Powder NiAl H.C. Starck, plasma power 25 kW, plasma gas composition Ar:H_2:He 45:4:10, Vacuum pressure: ambient pressure, layers sprayed: 14, scan speed: 400 mm/s, heating: 200°C.*$_{sample\ RES\text{-}El62}$*.*
Red dot: project target value corresponding to an efficiency of 80% on HHV basis at 0.75 A/cm^2.

4. Conclusions and outlook

Electrodes with a high efficiency could be coated by Vacuum Plasma Spraying and tested in a 300 cm^2 single cell.
It was planned to use these electrodes also for supply to the stacks of the project. However for two reasons the coating parameters for the stack electrodes (see deliverable report D4.3) had to be slightly different from the electrodes in this report:
For the cathode it was found that when coating a large area, as it is done when 8 electrodes of 300 cm^2 size are coated in one batch, the powder deposit is not constant. At atmospheric pressure in the chamber the nozzle used is getting clogged repeatedly for a short moment with big lumps of powder being applied

after that. The coating is not getting smooth and homogeneous. For only a shorter time of operation of the plasma torch this doesn't happen. Therefore the stack electrodes were coated with only a thin layer of the anode coating as described here and subsequent an anode coating sprayed in vacuum (see deliverable report D4.2).
For the cathodes there was not enough material NiAlMo by Sulzer available to coat the many stack electrodes. Sulzer-Metco could not supply more of it. Commercially available is a spray-dried NiAlMo pulver by H.C. Starck, that could be purchased with the composition of 16.8 wt% Mo, 38.9 wt% Ni, 44.3 wt% . This differs only slightly from the Sulzer powder, however the particle size and phase composition is clearly different. Similar to the NiAl powder from the same supplier used for the cathode the NiAlMo has a maximum of the particle diameter distribution at 22 µm, with most of the particles being between 6 and 32 µm. The SEM image also shows some big balls but many more small balls than for the Sulzer powder. Microscope images of the electrode coating cross section show a higher porosity of the layers with H.C. Starck powder due to the different particle size distribution. This could be of disadvantage for the mechanical stability of the layer. The XRD spectrum is shown in Figure 10. According to the phases peak fit the relative content ot this powder of the alloy phase Al_3Ni_2 is lower. This is the phase of which Al can most easily be removed by leaching [Kayser92, Bradke89], so that a lower content of this phase is not desirable. However still good electrode coatings can be made with H.C. Starck NiAlMo powder. This is also shown by the measurements with DLR coated electrodes performed in a 25 cm^2 cell at FZ Juelich that used H.C. Starck NiAlMo powder for the cathode coating. These measurement showed very low cell voltages.

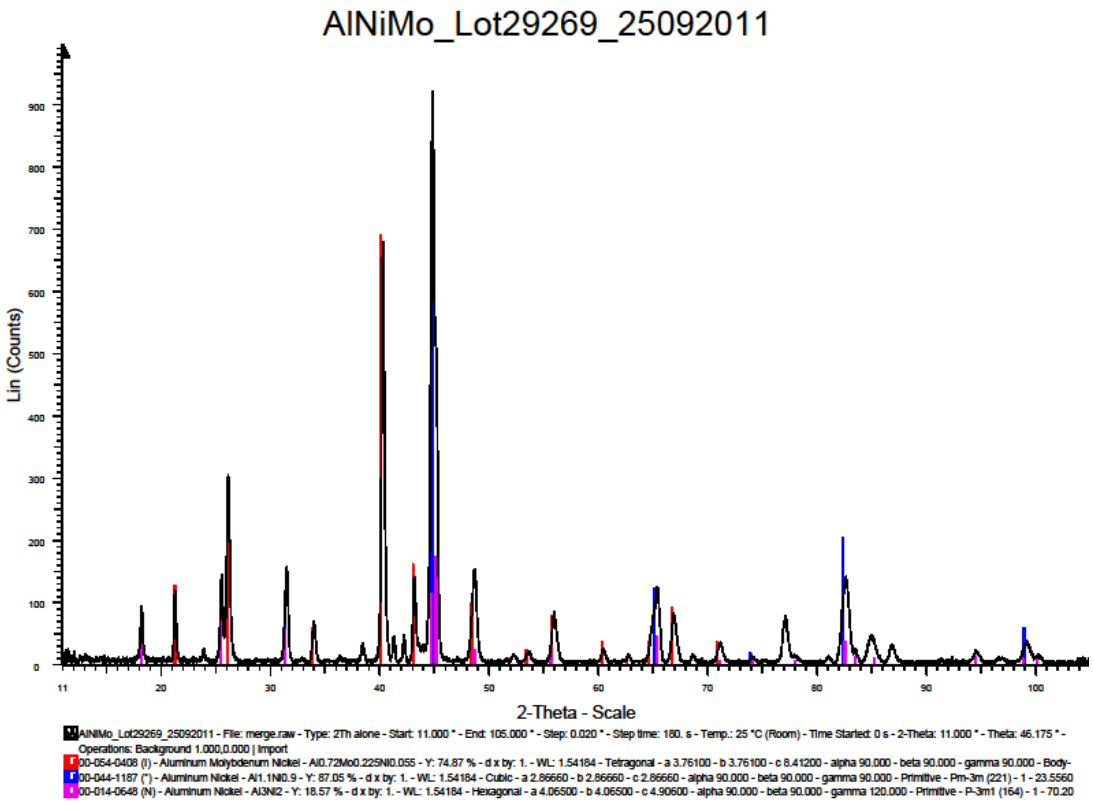


Figure 10: XRD spectrum of NiAlMo powder by H.C. Starck for VPS coating. The phases $Al_{0.72}\,Mo_{0.225}\,Ni_{0.055}$, $Al_{1.1}\,Ni_{0.9}$ and Al_3Ni_2 fit to the data are shown.

5. Literature references

[Carmo15] M. Carmo, FZ Jülich, private communication
[Kayser92] A. Kayser et al, Z. Metallkd. 83 (1992) (7) 565
[Bradke89] M. v.Bradke, W. Schnurnberger, I. Seybold, „Feinstruktur der Oberflächen von Raney_Nickel Elektroden“, Proceed. Elektronenmikroskop. Direktabb. Ofl. 22 (1989) 78-88

6. Appendix

Summary of electrodes sprayed and investigated either by half cell or full cell test or by microscopy

Name Elec-trode	VPS-Nr.	Short summary composi-tion	Descrip-tion of micro-scope image cross sec-tion	IR-corrected mV at 500mA/cm2 in 30% KOH, 70°C; rel. Hg/HgO	IR-corrected mV at 500mA/cm2 in 30% KOH, 70°C; rel. H2 rev	Stability few days	layer thick-ness um

Cathodes:							
RES-Ni177		velocity 100, less layers, heating plate with frames 400°C .	very porous, layered pores, po-rous link to substrate, surface rough				142
RES-Ni178		velocity 100, less layers, heating plate with frames 400°C	very porous, layered pores, po-rous link to substrate, surface rough			detached after OCV 3 days	144
Probe Schwan 4							
Probe Schwan 5							
RES-Ni181		velocity 100, less layers, heating plate with frames 400°C	very porous, layered pores, po-rous link to substrate, surface rough, Many bright pan-cakes in NiAl				153
RES-Ni87		velocity 100, less layers, heating plate with frames 400°C, then rolled					
RES-Ni91		velocity 100, less layers, heating plate with frames 400°C	partially layered pores	-1150			
RES-Ni92		velocity 100, less layers, heating plate with frames 400°C		-1004		2 Months	
RES-Ni93		velocity 100, less layers, heating plate with frames 400°C		-996			

RES-Ni55		velocity 100, less layers, heating plate with frames 400°C	somewhat layered , in the layer very dense	-1058 in 35%			179
RES-Ni143		Standard		-1002		12 days, then some pieces, operated for 20 days	
RES-Ni130		Standard		-1028		1 month, still complete but worse	
RES-Ni131		Standard					
RES-Ni54		Standard	well baked, pore inclu-sions, top layer broken				125
RES-Ni134		7mm-nozzle without intermedi-ate layer	fine cracks between the pancakes	-1008		becomes quickly defi-nitely worse, pieces de-tached	
RES-Ni119		thinner		-1012		after 2 weeks 100 mV worse, still complete	
RES-Ni139		only NiAl atmosperi-cally spra-yed	quite small regions very badly con-nected	-1068		only shortly tested as H2 electrode	
RES-Ni157		NiAlMo Sulzer, 28 kW	well con-nected with big holes included	-989		9 days opera-tion, rather constant values	
RES-Ni 184		NiAlMo Sulzer, 90°C activated; possibly impurities			-101	after 11 days 60 mV de-gradation	
RES-Ni 185	3.13.0189	NiAlMo Sulzer; possibly impurities			-110	no longer test	
RES-Ni 186		NiAlMo Sulzer; possibly impurities; 90°C acti-vated			-97	after 11 days 110mV de-gradation	

RES NI -202	3.13.0008	NiAlMo Starck/NiAl 25 kW 100 mm/s re-producibil-ity test			-82	some degra-dation with time; few days	
RES NI -207	3.13.0012	NiAlMo Starck/NiAl 25 kW 100 mm/s re-producibil-ity test					
RES NI -207	3.13.0012	NiAlMo Starck/NiAl 25 kW 100 mm/s re-producibil-ity test			-91	few days; stable	
RES NI -208	3.13.0012	NiAlMo Starck/NiAl 25 kW 100 mm/s re-producibil-ity test			-89	?	
RES NI -209	3.13.0012	NiAlMo Starck/NiAl 25 kW 100 mm/s re-producibil-ity test			-99	not clear	
RES Ni 188	3.13.0199	NiAlMo Starck/NiAl 25 kW 100 mm/s					
RES Ni 189	3.13.0199	NiAlMo Starck/NiAl 25 kW 100 mm/s					
RES Ni 190	3.13.0199	NiAlMo Starck/NiAl 25 kW 100 mm/s					
RES Ni 191	3.13.0199	NiAlMo Starck/NiAl 25 kW 100 mm/s					
RES Ni 192	3.13.0199	NiAlMo Starck/NiAl 25 kW 100 mm/s					
RES Ni 193	3.13.0199	NiAlMo Starck/NiAl 25 kW 100 mm/s					
Res Ni 194	3.13.0200	NiAlMo Starck alt/NiAl 25 kW 400 mm/s 7 mm nozzle					

Res Ni 195	3.13.0200	NiAlMo Starck alt/NiAl 28 kW 400 mm/s 7 mm nozzle					
Res Ni 196	3.13.0201	NiAlMo Starck old and new?/NiAl 18 kW 100 mm/s 7mm nozzle					
Res Ni 197	3.13.0201	NiAlMo Starck old and new?/NiAl 18 kW 100 mm/s					
RES NI -200	3.14.0008	NiAlMo Starck/NiAl 25 kW 100 mm/S re-producibil-ity test			-81	only short test	
RES NI -201	3.14.0008	NiAlMo Starck/NiAl 25 kW 100 mm/S re-producibil-ity test			-85	?	
Res Ni 203	3.14.0009	NiAlMo Sulzer/NiAl 28 kW 600 mm/s			-86	well constant	
Res Ni 204	3.14.0009	NiAlMo Sulzer/NiAl 28 kW 600 mm/s 90° leached			-87	well constant	
Res El 65	3.14.0009	NiAlMo Starck/NiAl 28 kW 600 mm/s; large electrode, punched hole sheet					
Res El 66	3.14.0009	NiAlMo Starck/NiAl 28 kW 600 mm/s; large electrode					
RES-El 67	3.14.0010	NiAlMo Starck/NiAl 28 kW 600 mm/s; large electrode					

RES NI -205	3.14.0011	only nickel coated, 25 kW, 400 mm/s					
RES NI -206	3.14.0011	only nickel coatedt, 25 kW, 400 mm/s					
RES-CF -5	3.14.0014	NiAlMo Starck 25 kW 45 Ar					
RES-CF -6	3.14.0014	NiAlMo Starck 27 kW 65 Ar, longer distance					
RES-CF -7	3.14.0014	NiAlMo Starck 36 kW 65 Ar, longer distance					
RES-CF -8	3.14.0014	NiAlMo Starck 42 kW 65 Ar, longer distance					
RES-Ni -210	3.14.0015	NiAlMo Starck 25 kW 45 Ar . . .	many medium sized pores, no thin long pores parallel to surface				
RES-Ni -211	3.14.0015	NiAlMo Starck 27 kW 65 Ar, longer distance	many medium sized pores (more), no thin long pores parallel to surface				
RES-Ni -212	3.14.0015	NiAlMo Starck 36 kW 65 Ar, longer distance	many medium sized pores (less), no thin long pores parallel to surface				
RES-Ni -213	3.14.0015	NiAlMo Starck 42 kW 65 Ar, longer distance	many medium sized pores (less), no thin long pores parallel to surface				
RES_CF -9	3.14.0016	NiAlMo Starck 1% V2O5, NiAl Starck, 100 mm/s					
RES_CF -10	3.14.0016	NiAlMo Starck 1% V2O5, NiAl Starck , 400					

		mm/s					
RES_CF -11	3.14.0017	NiAlMo Starck 5% V2O5, NiAl Starck, 100 mm/s					
RES_CF -12	3.14.0017	NiAlMo Starck 5% V2O5, NiAl Starck , 400 mm/s					
RES_CF -13	3.14.0018	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 100 mm/s					
RES_Ni -214	3.14.0018	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 100 mm/s			-84	?	
RES_CF -14	3.14.0018	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 400 mm/s					
RES_Ni -215	3.14.0018	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 400 mm/s			-84	some degra-dation with time	
RES_CF -15	3.14.0019	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 100 mm/s					
RES_Ni -216	3.14.0019	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 100 mm/s			-86	?	
RES_CF -16	3.14.0019	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 400 mm/s					

RES_Ni -217	3.14.0019	NiAlMo Starck 5% V2O5, NiAl Starck 5% V2O5, 400 mm/s			-90	improveme-ment with time, few days	
RES_Ni -218 (b)	3.14.0020	NiAlMo Sulzer, NiAl, 42 kW, Ar 65 (more), H2 4 (less), He 10			-90	11th day clearly de-graded	
RES_Ni -219 (B)	3.14.0020	NialMo Sulzer, NiAl, 42 kW, Ar 65, H2 4, He 10; bei 90° leached			-93	rel constant	
RES-EL Ø70mm -2	3.14.0022	NiAlMo Sulzer, NiAl, 28 kW, punced hole sheet, larger					
RES Ni218	3.14.0032	NiAlMo Starck 1% V2O5, NiAl 1% V2O5			-82	becomes a little better	
RES Ni219	3.14.0032	NiAlMo Starck 1% V2O5, NiAl 1% V2O5 25 kW 100 mm/s			-85	rel. konstant	
RES Ni220	3.14.0032	NiAlMo Starck 1% V2O5, NiAl 1% V2O5 25 kW 400 mm/s					
RES_Ni 221	3.14.0033	NiAlMo Starck 5% V2O5, NiAl 5% V2O5, 25 kW, 400 mm/s			-86	rel. constant few days	
RES_Ni 222	3.14.0033	NiAlMo Starck 5% V2O5, NiAl 5% V2O5, 25 kW, 400 mm/s			-89	rel. konstant	
RES_Ni 223	3.14.0033	NiAlMo Starck 5% V2O5, NiAl 5% V2O5, 25 kW, 400 mm/s					

RES_CF	3.14.0064	NiAlMo Sulzer/NiAl 28 kW, 600 mm/s					
RES_Lochblech	3.14.0064	NiAlMo Sulzer/NiAl 28 kW, 600 mm/s; Auftrag					
Res_Ni -224	3.14.0064	NiAlMo Sulzer/NiAl 28 kW, 600 mm/s . . Leached 90°	layer rather dense but not every-where. After leaching 90°C opera-tion 1st, 2nd, 12th day + on-off under frame spongelike porous, partially large cracks			leached 90°C, after 12 days increas-ing delamina-tion in medi-um size pieces, NiAl layer remains partially	80
Res_Ni -225	3.14.0064	NiAlMo Sulzer/NiAl 28 kW, 600 mm/s . .leached 90°, 1 wet in air, oper-ated 1., 2., 12. Tag	layer dense with inclu-sions, sur-face very rough. 90° leached and operated shows many wide long pores				75
Res_Ni -226	3.14.0064	NiAlMo Sulzer/NiAl 28 kW, 600 mm/s . leached RT, operated at 70°C					
Res_Ni -227	3.14.0064	NiAlMo Sulzer/NiAl 28 kW, 600 mm/s					
RES_Ni -228	3.14.0065	NiAlMo Sulzer/NiAl 41 kW . . .	layer dense but still some inclu-sions				95
RES_Ni -229	3.14.0065	NiAlMo Sulzer/NiAl 41 kW					

RES Ni Ref1	3.14.0075	NiAlMo Starck/NiAl 28kW 600mm/s coated together with large electrodes, preheated with burner	fine long pores paral-lel to sur-face, some inclusions, rough sur-face				75
RES CF Ref1	3.14.0075	NiAlMo Starck/NiAl 28kW 600mm/s coated with large elec-trodes, preheated with burner					
RES El 67 - 74	3.14.0075	NiAlMo Starck/NiAl 28kW 600mm/s , preheated with burn-er. Large electrode for stack					
RES CF Ref2	3.14.0076	NiAlMo Starck/NiAl 28kW 600mm/s , together with large stack elec-trodes, preheated with burner					
RES El 75-82	3.14.0076	NiAlMo Starck/NiAl 28kW 600mm/s ,preheated with burn-er. Large electrode for stack					
RES CF Ref3	3.14.0077	NiAlMo Starck/NiAl 28kW 600mm/s , together with stack electrodes, preheateg with burner					

RES El 83-90	3.14.0077	NiAlMo Starck/NiAl 28kW 600mm/s , preheated with burner. Large electrode for stack					
RES CF Ref4	3.14.0078	NiAlMo Starck/NiAl 28kW 600mm/s , coated together with stack electrodes. Preheated with burner					
RES El 91-96	3.14.0078	NiAlMo Starck/NiAl 28kW 600mm/s , preheated with burner. Large electrode for stack					
RES Ni Ref 2	3.14.0078	NiAlMo Starck/NiAl 28kW 600mm/s , coated together with stack electrodes, preheated with burner	fine long pores parallel to surface, some inclusions, rough surface		-89.3		57
NEM 101213		Nickel substrate uncoated, sand blasted			-286		
NEM110314		Nickel substrate uncoated (sand-blasted?)			-370		
NEM090315	uncoated	NEM sand blasted, 1st day			-327		
NEM090315	uncoated	NEM sand blasted, 4th day, before O2 operation			-227		

NEM060315	uncoated	NEM sand blasted, day 2, before O2 opera-tion			-262		
RES-Ni1501-11	3.15.0010	NiAlMo, more gases, Ni layer			-85		
RES-Ni1501-18							
NEM080415	-	uncoated, not treated			-359		
Anoden							
RES-Ni139		only NiAl atmo-spherical coating		541		after 1 month worse, some pieces de-taching	
RES-Ni139		NiAl+Co3O4 atmosphä-risch		511		fine dust	
RES-Ni140							
RES-CF -1	3.14.0013	NiAl 25 kW 45 Ar . . .	many medi-um size pores, no thin long pores paral-lel to surface				
RES-CF -2	3.14.0013	NiAl Starck 27 kW 65 Ar, larger distance	more medi-um sized pores, no thin long pores paral-lel to surface				
RES-CF -3	3.14.0013	NiAl Starck 36 kW 65 Ar, larger distance	more medi-um sized pores, no thin long pores paral-lel to surface				
RES-CF -4	3.14.0013	NiAl Starck 42 kW 65 Ar, longer distance	some medi-um sized pores, hard-ly better than 25 kW, no thin long pores paral-lel to surface				
RES-El -64	3.14.0007	NiAl 25 kW atm; large electrode					
RES- Ni -198	3.14.0007	NiAl 25 kW atm					
RES- Ni -199	3.14.0007	NiAl 25 kW					

		atm					
RES-El -62	3.14.0006	NiAl atm; large electrode					
RES-El -63	3.14.0006	NiAl atm; large electrode					
RES- Ni -230	3.14.0066	NiAl atm			1.5	layer detach-es but per-formance still ok. Long operation also on-off	
RES- Ni -231	3.14.0066	NiAl atm					
RES- Ni -232	3.14.0066	NiAl atm					
RES- Ni -233	3.14.0066	NiAl atm					
RES- Ni -234	3.14.0066	NiAl atm, substrate only sand blasted					
RESNi169	3.13.0184	NiAl+30% Ni, VPS; impurities?; Tag 1	Ni forms no matrix		1.55		
RES-NiRef3	3.14.0080	NiAl 25 kW first atmos-pheric, then VPS , coated together with stack electrodes, preheated with burn-er. Before old coating removed by sand blast-ing. Nozzle sometimes clogged; day 1	Some pores included. Bottom atmospheric layer very grainy and many pores		1.522		
RES-NiRef3	3.14.0080	NiAl VPS + atm coated with stack electrodes; day 3			1.544		
RES-Ni 206	3.14.0011	Ni coating			1.56		
RES-Ni 160	3.13.0172	NiAL VPS/NiAl atm; 1st day			1.52		
RES-Ni 160	3.13.0172	NiAL VPS/NiAl atm; 10th day			1.56		

RES-Ni 160	3.13.0172	NiAL VPS/NiAl atm; after 11 months, 1 day in air, long OCV RT			1.441		
RES-Ni 159	3.13.0172	NiAl atm			1.53		
REG_Co3O4AgAgN_01		GDE battery Ag + Co3O4; instable voltage			1.52		
NiH3		GDE Ni old		650	1.571		
Silva 8s		GDE Ag old			1.61		
RES-Ni 1501-6	3.15.0007	NiAl / Ni intermedia-te layer			1.53		
	3.14.0021						
RES-EL Ø70mm -1		NiAl atm, punched hole sheet, larger					
NEM090315	unbe-schichtet	NEM sand-blated, 1st day			1.592		
NEM090315	unbe-schichtet	NEM sand-blasted, O2- and H2-operation, 2nd day			1.617		
NEM060315	unbe-schichtet	NEM san-blasted stored in air, 1st day			1.573		
NEM060315	unbe-schichtet	NEM sand-blsted, day 3 (no H2-operation)			1.612		
RESNi1501-6	3.15.0007	NiAl more gases, Ni layer			1.538		
NEM270315	unbe-schichtet	Uncoated, not pre-treated, visible oxide; day 1			1.66		

RES CF Ref5	3.14.0080	NiAl 25 kW first atmospheric, then VPS , coated togehter with stack electrodes, preheated with burner. Before old coating removed by sand blasting. Nozzle sometimes clogged					
RES El 97-104	3.14.0080	NiAl 25 kW first atmospheric, then VPS , coated togehter with stack electrodes, preheated with burner. Before old coating removed by sand blasting. Nozzle sometimes clogged					
RES CF Ref5	3.14.0081	NiAl 25 kW first atmospheric, then VPS , coated togehter with stack electrodes, preheated with burner. Before old coating removed by sand blasting. Nozzle sometimes clogged					

RES El 105-112	3.14.0081	NiAl 25 kW first atmos-pheric, then VPS , coated togehter with stack electrodes, preheated with burn-er. Before old coating removed by sand blast-ing. Nozzle sometimes clogged. Large electrode for stack					
RES CF Ref7	3.14.0082	NiAl 25 kW first atmos-pheric, then VPS , coated togehter with stack electrodes, preheated with burn-er. Before old coating removed by sand blast-ing. Nozzle sometimes clogged					
RES El 113-120	3.14.0082	NiAl 25 kW first atmos-pheric, then VPS , coated togehter with stack electrodes, preheated with burn-er. Nozzle sometimes clogged. Large electrode for stack					

RES Ni Ref4	3.14.0083	NiAl 25 kW first atmospheric, then VPS , coated togehter with stack electrodes, preheated with burner. Nozzle sometimes clogged.	Some pores included. Bottom layer sprayed atmospherically very grainy and high porosity				68
RES CF Ref8	3.14.0083	NiAl 25 kW first atmospheric, then VPS , coated togehter with stack electrodes, preheated with burner. Nozzle sometimes clogged.					
RES El 121-128	3.14.0083	NiAl 25 kW first atmospheric, then VPS , coated togehter with stack electrodes, preheated with burner. Nozzle sometimes clogged.					