

## **A Proof-of-Principle Demonstration: Exploring the Effect of Anode Layer Microstructure on the Alkaline Oxygen Evolution Reaction**

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Keywords: drying process, morphology, ultrasonic spray coating, catalyst layer, Cassie-Baxter model, oxygen evolution reaction, alkaline water electrolysis

This study explores the effect of Ni-Co-O anode layer microstructure on the oxygen evolution reaction (OER). Four anodes with similar Ni-Co-O loadings and chemical characteristics but distinct morphologies are fabricated by ultrasonic spraying catalyst inks of varying solvent composition (pure water vs a water-ethanol mixture) and drying temperatures (50 °C and 150 °C) on Ni plates. Upon varying solvent composition, particles in the water-based ink exhibited lower stability than particles in the water-ethanol-based ink, boosting the particle connectivity in the layers. This particle connectivity correlated with the mechanical strength of the layers, resulting in reduced contact resistance and enhanced activity. Our second observation is that at 50 °C, the surface morphology exhibited hill-like islands with higher roughness, while at 150 °C, concave hemispherical shapes with lower roughness were observed. From 2D-distribution data, we found that surface roughness correlated with the wettability with electrolyte. Roughness increased the lyophobicity and enhanced the activity through more accessible active sites and efficient bubble transport. Taken together, this work highlights how microstructure affects macroscopic layer properties, and how these in turn can enhance or diminish the performance of the OER compared to bare nickel, offering insights into the knowledge-based design of anode layers.

## **1. Introduction**

The oxygen evolution reaction (OER) in alkaline water electrolysis (AWE) involves a three-phase contact line,<sup>[1]</sup> where the electrolyte in the liquid phase serves as a reactant, oxygen produced exists in the gas phase, and the solid phase comprises the catalyst coated-anodes, i.e., anode layers. This contact line is governed by complex flow and transport dynamics, including the drainage of oxygen, paths for electron transportation and the invasion of reactants.<sup>[2]</sup> Nano-powdered catalysts have attracted significant interest in anode layer fabrication due to their remarkable ability to form specific structures or morphologies.<sup>[3]</sup> In particular, the precise, stable, and controllable assembly of nanoparticles on anode supports is crucial for achieving electrocatalytic functionality at the three-phase contact line.<sup>[4]</sup> Despite the importance of layer microstructure in solid-phase applications, their systematic design and targeted modification remain largely underexplored. Fabrication process conditions critically define the finally obtained microstructural features including surface roughness, particle distribution, particle connectivity, porosity, pore size distribution, pore connectivity and tortuosity. However, the precise relationships and mechanisms underlying these effects are not well-defined. Moreover, it is still unclear how these microstructures can be translated into macroscopic layer properties like wettability and mechanical stability, and how these

macroscopic layer properties ultimately affect the oxygen evolution reaction (OER). We believe that bridging these knowledge gaps, from microstructure to layer properties and from layer properties to electrochemical performance is essential, in particular during scale-up, for the rational design of advanced alkaline anodes with enhanced OER efficiency.

For tuning the microstructure of layered nanoarchitectures, nanoparticles and their assemblies typically serve as the fundamental building blocks. While nanoparticles are often generated by sol-gel, co-precipitation, hydrothermal and solvothermal synthesis, thermal decomposition and spray pyrolysis up to the industrial scale,<sup>[5]</sup> their directed assembly in nanostructured layers is an ongoing challenge. Recent studies have explored various methods to design and configure microstructure from the assembly of nanoparticles.<sup>[6]</sup> On laboratory scale, thermodynamically driven self-assembly utilizes natural interparticle forces such as van der Waals forces, electrostatic interactions, and hydrogen bonding, enabling the spontaneous organization of nanoparticles into ordered structures.<sup>[7]</sup> This method leverages the inherent properties of the particles and their environment to achieve a desired nanoarchitected microstructure without external intervention. In contrast, indirect assembly employs the involvement of external forces such as electric or magnetic field-directed assemblies, fluid flow-induced assemblies, or evaporation-induced assemblies and these have been utilized for scale-up.<sup>[8]</sup> Many indirect techniques and processes adapted from traditional technologies exist in painting, printing, and metal decoration. For instance electroplating, spray coating, and ink-jet printing offer viable options for applying a thin layer onto the intended supports.<sup>[9]</sup> For anode formation in alkaline electrolysis, the indirect assembly of nanoparticles is – amongst other technologies<sup>[10]</sup> – applied for the deposition of catalyst particles onto support materials such as plates, meshes and foams, ensuring proper adhesion and functionality.<sup>[11]</sup> However, despite many researchers utilized these techniques to fabricate anode layers for water splitting, the correlation between microstructure, anode layer wetting, mechanical strength and electrochemical performance is still concealed.

In this study we adjusted the microstructure of four anode layers by applying two different solvent compositions commonly utilized for transition metal oxide based inks during ink formulation,<sup>[12]</sup> pure water and a mixture of water and ethanol. These were applied at two different drying temperatures, 50 °C and 150 °C, during ultrasonic spray coating. We demonstrated how catalyst stability correlates with the solvent composition using transmittogram and S-score analyses from stability trajectories developed by us.<sup>[13]</sup> The fabricated microstructure of the anode layers was characterized and quantified by top view scanning auger electron microscopy (SAM), topographical atomic force microscopy (AFM),

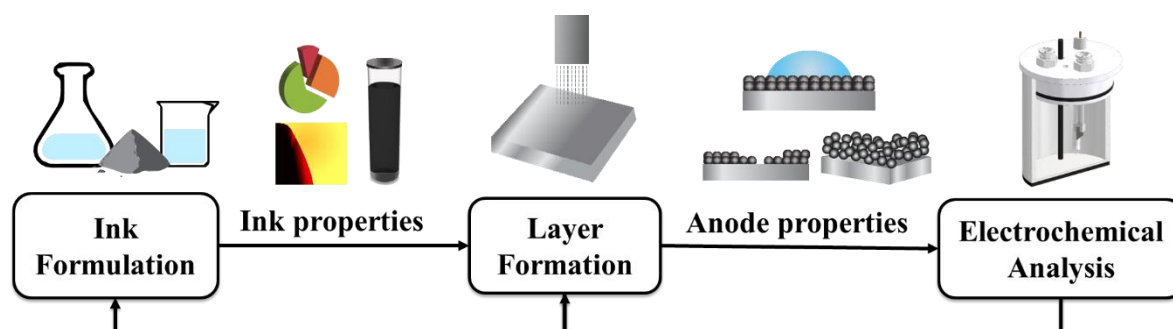
and cross-sectional focused ion beam scanning electron microscopy (FIB-SEM).

Subsequently, we analyzed the correlation between the microstructure and the two key anode layer properties: wetting and mechanical strength of the layers. Upon having access to these usually unknown properties, ultimately, we were able to correlate the microstructure of the generated anodes with their wetting and mechanical strength, and to further connect these properties with beaker cell electrochemical activity and stability data. Taken together, our approach enables to decipher the process-microstructure-property-performance relationships that are crucial to enhance electrochemical processes and mechanisms<sup>[14]</sup>.

## 2. Results and Discussion

### 2.1 Strategy for the rational design of anode layers with electrochemical assessment

First, a strategy was developed that enables to correlate microstructure with electrochemical performance. The challenge was to fabricate anode layers that vary in the decisive properties such as surface roughness, wetting behavior, and mechanical strength, while maintaining comparable mass loading and constant chemical composition. The fabrication strategy is delineated in Figure 1. It illustrates the progression from the selection of the necessary components to electrochemical performance testing and can be divided into three main stages: an ink formulation stage, a layer formation stage and an electrochemical analysis stage. Each stage presents specific challenges, and advancing through the entire process chain is labor-intensive, yet essential for elucidating the underlying process-microstructure-property-performance relationships.<sup>[14,15]</sup>



**Figure 1.** Schematic representation of the developed strategy for the fabrication, microstructure and property assessment of anode layers, including ink formulation, layer formation by coating, microstructure assessment and electrochemical analysis.

In the initial stage, to investigate the impact of the carrier liquid on the structure and property of the layers, we prepared two catalyst inks: one with water and the other with a 1:1 mixture

of water and ethanol, utilizing nickel cobalt oxide as the catalyst and Nafion as the binder.<sup>[16]</sup> Subsequently, we examined the dispersibility and stability of the prepared inks.

In the second stage, the analyzed inks were deposited on a nickel plate, i.e., the anode support, by ultrasonic spray coating. To unravel the effect of flow- and evaporation-induced nanoparticle-assembly on the anode support, we set two distinct heating temperatures: 50 °C, which is a considerable temperature to evaporate inks near to atmospheric conditions and 150 °C, which is larger than the boiling points of the utilized carrier liquids. At this point, it should be noted that the glass transition temperature of Nafion occurs at around 130 °C.<sup>[17]</sup> At temperatures slightly above this point, the polymer transitions from a glassy to a rubbery or viscous state, which is further influenced by the swelling of Nafion in the presence of alcohol.<sup>[18]</sup> However, after the drying process, Nafion is expected to regain its original chemical composition, as it maintains chemical stability up to 280 °C.<sup>[19]</sup> In this work, we introduced Nafion – though being designed for proton, not for hydroxyl ion transport – to enhance the mechanical stability of the layers. In the following, we refer to the water-based ink applied at 50 °C as W-50C and at 150 °C as W-150C. Similarly, the ink made with the water-ethanol mixture as continuous phase applied at 50 °C is denoted as WE-50C, and at 150 °C as WE-150C.

In the second stage, we subsequently analyzed the microstructure of the four resulting anodes and related them with macroscopic layer properties like the initial wetting with the electrolyte (lyophilicity/lyophobicity) and mechanical stability.

In the last stage, we utilized a beaker cell setup to evaluate the electrochemical activity and stability of the four anodes, W-50C, W-150C, WE-50C and WE-150C.

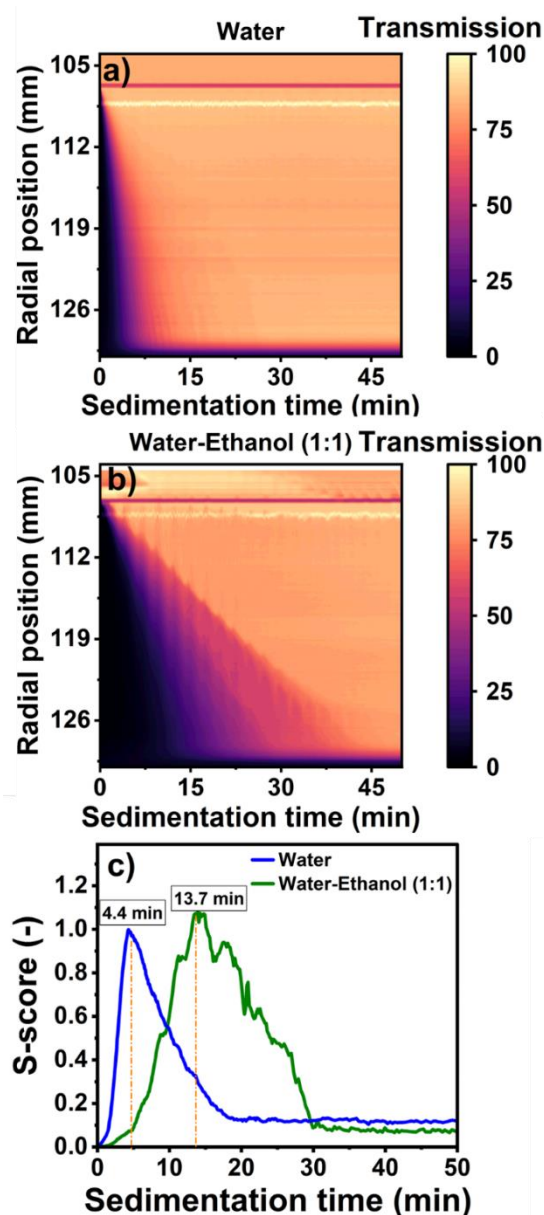
This methodology enabled us to discern the significance of solvents and drying temperatures on layer properties and, ultimately, on electrochemical performance. The detailed experimental setups and parameters are described in the Experimental section.

## **2.2 Microstructure formation and assessment**

### *2.2.1 Catalyst ink properties*

Figure 2 illustrates the sedimentation of catalyst nanopowders in water and water-ethanol with Nafion binder. The ink dispersions were analyzed using transmittograms, which in brief enable the direct visualization of the transmittance along the radial position of the measurement cell over the sedimentation time (Figure 2a-2b) and can be further evaluated through S-scores as stability-metric, both recently developed by us (Figure 2c).<sup>[13]</sup> By analyzing the characteristic patterns during the sedimentation process, the initial dispersion

state, formulation stability against agglomeration, interaction of catalyst materials, and lifespan of the inks can be assessed.



**Figure 2.** Visualization of the time-resolved sedimentation process via transmittograms: (a) Ink prepared using pure water as a solvent, (b) ink prepared using a mixture of water and ethanol as continuous phase (1:1 ratio) and (c) direct comparison of both inks via stability trajectories.

The transmittograms in Figure 2(a-b) show a distinct difference in the sedimentation behavior between the two formulations. For pure water (Figure 2a), the sedimentation is relatively rapid, with high transmission levels observed early on and minimal gradient formation, indicating fast settling of particles. In contrast, using the water-ethanol mixture as continuous phase (Figure 2b) results in a slower sedimentation process, with a more gradual transmission

gradient over time, suggesting a slower settling rate. This difference is quantitatively analyzed by the stability trajectory shown in Figure 2c. The S-score for water shows a sharp maximum at 4.4 minutes, where the bulk sedimentation occurs, which represents the maximum of particles that are sedimented at this point, indicating rapid sedimentation. The complete sedimentation of the particles occurred approximately 20 minutes at the relative centrifugal acceleration (RCA) of 733.69, which is equivalent to 10 days and 11 hours in real-time stationary conditions (RCA = 1). For the water-ethanol mixture, the sedimentation process is more prolonged, with the S-score reaching its bulk sedimentation at 13.7 minutes. The sedimentation of all particles occurred approximately after 30 minutes, which is equivalent to 15 days and 6 hours at RCA = 1. Noteworthy, the addition of Nafion as a binder did not affect the sedimentation behavior and thus the stability of the ink formulations, as highlighted by the S-score before and after its addition in Figure S1b. Although this result was unexpected, it can be explained by the lack of specific affinity of Nafion to the particle surface, indicating no significant chemisorption and likely no pronounced physisorption. This suggests that the stability of the inks is predominantly governed by the solvent composition rather than the presence of Nafion. The effect of key properties of the continuous phase, such as viscosity and density can be evaluated in combination as defined by Süß et al.<sup>[20]</sup> This is accomplished by determining the relative sedimentation time (RST) at bulk sedimentation. Determined  $RST_{BST}$  along with carrier liquids properties are shown in Table 1. The pure water-based ink has an  $RST_{BST}$  of  $5.48 \times 10^{15} \text{ m}^{-2}$  and the water-ethanol-based ink has a significantly higher value of  $8.86 \times 10^{15} \text{ m}^{-2}$ . At constant catalyst particle size, the higher the  $RST_{BST}$ , the higher the stability of the formulation over time and the longer the shelf-life.

**Table 1.** Key physical properties: Viscosity ( $\eta$ ), density ( $\rho$ ) of carrier liquid, and relative sedimentation time at bulk sedimentation ( $RST_{BST}$ ) of the inks. Data was measured at 293 K.<sup>[21]</sup>

| Carrier liquids | $\eta \times 10^{-3} \text{ (Pa}\cdot\text{s)}$ | $\rho \times 10^3 \text{ (kg}\cdot\text{m}^{-3}\text{)}$ | $RST_{BST} \times 10^{15} \text{ (m}^{-2}\text{)}$ |
|-----------------|-------------------------------------------------|----------------------------------------------------------|----------------------------------------------------|
| Water           | 1.01                                            | 0.99                                                     | 5.48                                               |
| Water-Ethanol   | 2.37                                            | 0.85                                                     | 8.86                                               |

Taken together, the change in ink characteristics is mainly attributed to the different interactions of the particles with the carrier liquids used as continuous phase causing faster agglomeration in pure water and enhanced stability in water-ethanol mixtures. The overall

results highlight the significant impact of solvent composition and the interplay between solvents on sedimentation behavior, leading to a change in stability of the catalyst inks. Next, the analyzed inks were deposited on nickel plates for fabricating layers with different morphology. Given the high level of automation provided by the ultrasonic spray coating equipment employed in this study, all parameters, except the herein targeted solvent composition in the ink formulation and the drying temperature, could be kept constant (details are summarized in the Experimental section). In the following, the assessed microstructure of all four anodes will be discussed in detail.

### *2.2.2 Chemical properties of anode layers*

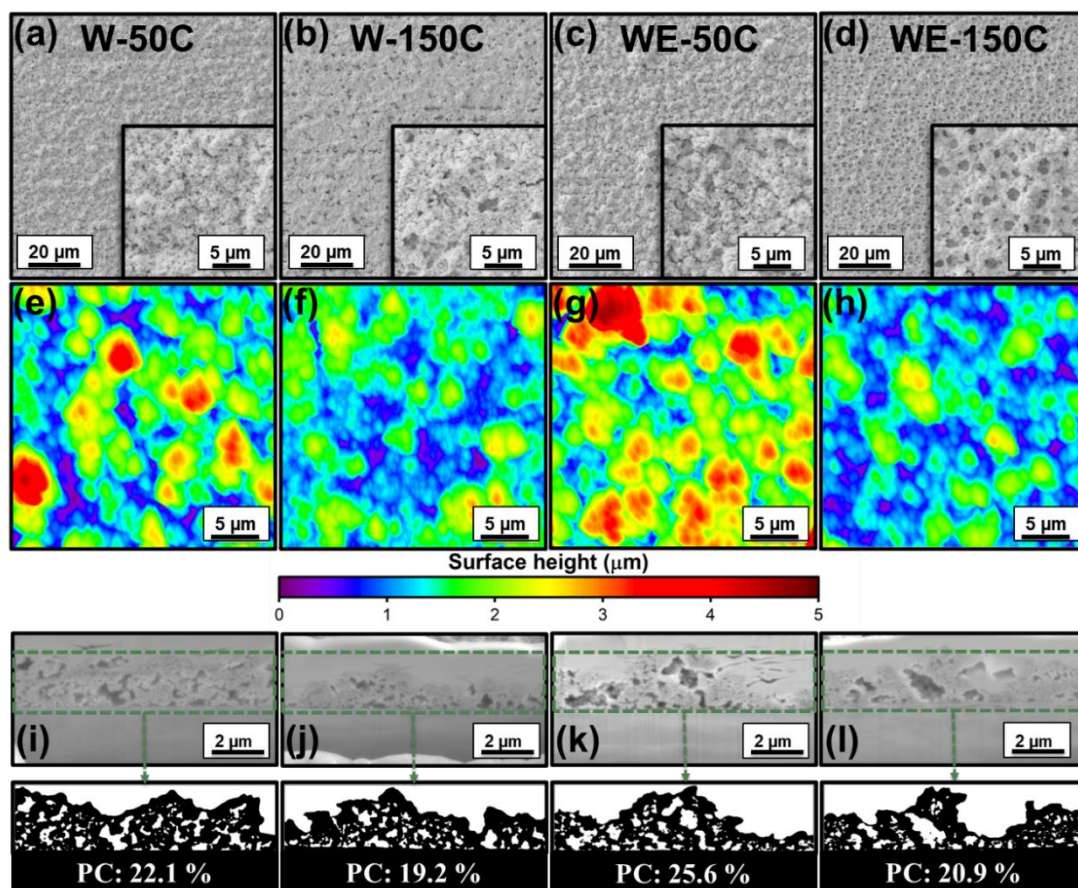
Investigating potential chemical changes during processing necessitated the employment of a wide range of analytical techniques, including Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The results obtained from each technique are discussed and summarized in supporting information section S2. By comparing results obtained from different complementary techniques (Raman, EDX, FTIR, and XPS), it can be concluded that the chemical nature of the as-obtained anodes including the chemical signature of the binder molecules, remains constant within the detection limits of the analytical devices across the varied processing parameters. Neither the drying temperature nor the solvent matrix utilized as continuous phase in the ink formulation showed a significant chemical impact. We ascribe this to the fact that the drying process was operated clearly below 280 °C, such that Nafion is expected to remain thermally stable. This absence of any change in the chemical properties is critical for comparing the different layers obtained here in terms of their microstructure and connecting microstructural changes with macroscopic layer and electrochemical properties.

### *2.2.3 Microstructure of the four anode layers*

Microstructure analyses in terms of the underlying surface morphology of the layers were performed utilizing top view scanning auger electron microscopy (SAM), topographical atomic force microscopy (AFM), and cross-sectional focused ion beam scanning electron microscopy (FIB-SEM). The results gained at high magnification above 1000x are depicted in Figure 3. Noteworthy, morphological analysis at low magnification, 100x (not shown) revealed that there is no evidence of cracks due to improper coating or drying on the surfaces. Already a first qualitative assessment of the gathered data revealed distinct surface morphologies between layers fabricated at lower temperatures (Figures 3a and 3c) and those



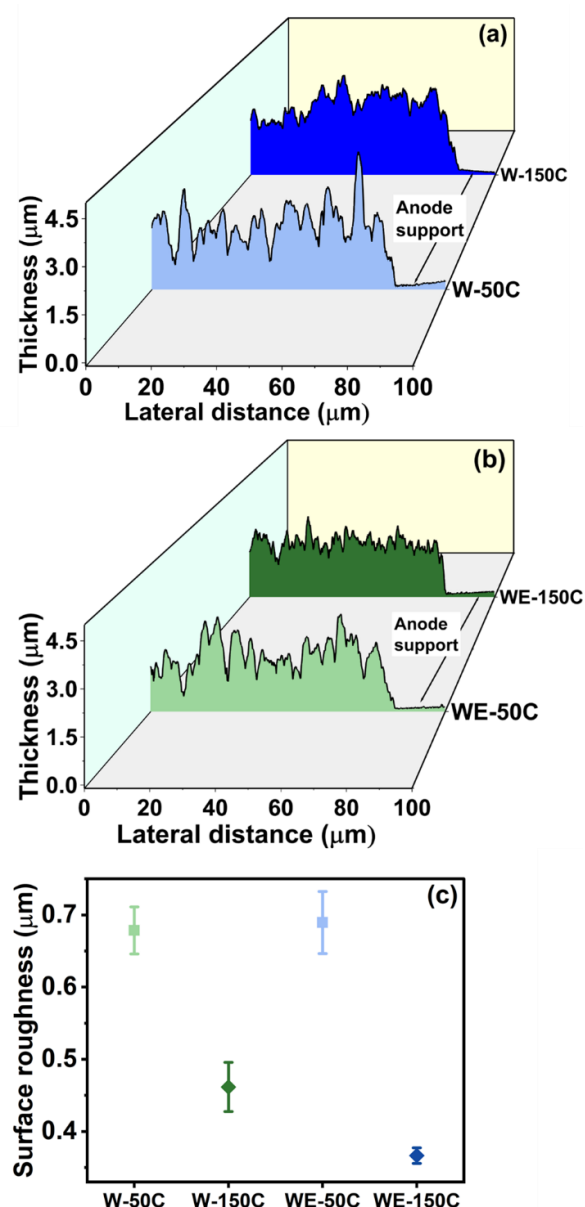
produced at higher temperatures (Figures 3b and 3d). Layers formulated with water-ethanol-based inks exhibited more defined and structured surface features compared to those prepared with water-based inks.



**Figure 3.** Morphology analysis using SAM: (a) W-50C, (b) W-150C, (c) WE-50C, (d) WE-150C. Morphology analysis using AFM: (e) W-50C, (f) W-150C, (g) WE-50C, (h) WE-150C. Cross-sectional analysis of anodes obtained using FIB-SEM along with binarized images of anodes and pore coverage (PC), which is defined as the area-percentage covered by pores in the cross-section: (i) W-50C, (j) W-150C, (k) WE-50C, (l) WE-150C.

Additionally, AFM characterization further revealed that at a lower drying temperature (50 °C), the anode surfaces displayed hill-like islands that are identifiable by the red color. These islands are ascribed to distinct assemblages that formed during coating and drying (Figures 3e and 3g). Conversely, at higher temperature (150 °C), the surfaces exhibited reduced island formation that is seen by the larger share of purple and blue regions (Figures 3f and 3h). Moreover, an ordered pattern with distinct motifs arises at higher temperature, which becomes particularly evident in case of WE-150C (Figure 3d). Closer analysis at higher resolution (insets of Figure 3b and especially of Figure 3d) indicates that the surface

morphology transitions to a concave, hemispherical shape. This shape resembles structures commonly seen in nature, such as the nest of a bird or a shallow pot. These are characterized by a curved inward surface that encloses a space, which provides an intuitive visualization of the observed concave morphology. These observations are in line with cross-sectional imaging data (Figure 3i-3l) that provided further insight into the depth profile of the fabricated anodes.



**Figure 4.** Surface features extraction from AFM data. Thickness of anode layer (a) W-50C and W-150C, as well as (b) WE-50C and WE-150C. Representative features extraction via MSDQ: Root mean square surface roughness (c).

However, since distinguishing the morphologies visually was challenging and inevitably remains subjective and in parts speculative, we applied image analysis (details are

summarized in the Experimental section) to quantify the differences. Specifically, the pore coverage was utilized to further compare the fabricated anodes. In brief, pore coverage is defined as the cross-sectional area covered by pores compared to the cross-sectional area covered by catalyst material. The determined pore coverage values for the layers are as follows: W-50C is 22.1 %, W-150C is 19.2 %, WE-50C is 25.6 %, and WE-150C is 20.9%. Here it is observed that the PC appears to be slightly higher for the layers fabricated at lower temperatures for both ink formulations.

To further underpin the quantitative analysis of microstructure, we extracted microstructural features such as surface roughness and homogeneity score as described in our previous work along with additionally measured thickness.<sup>[22]</sup> In brief, multi-stage data quantification (MSDQ) is a statistical framework that enables the extrapolation of surface features of a complete layer using targeted analyses from a representative amount of local regions (for details, refer to the Supporting Data, section S3). Here, thickness refers to the measured depth and valleys of the anode layer, surface roughness quantifies the average deviations in height, and the homogeneity score reflects the evenness of the surface across the analyzed area. These features were extracted using AFM to assess thickness, where a portion of the coated layer was removed to establish a baseline reference. These features are illustrated in Figure 4. Figure 4(a-b) shows the variations in peaks and valleys among the four fabricated anodes. W-50C and WE-50C exhibit elevated peaks and deeper valleys compared to W-150C and WE-150C. Figure 4c shows the increased surface roughness for the W-50C and WE-50C anodes compared to W-150C and WE-150C. In contrast, the inverse homogeneity score is expectedly larger due to the lower surface variation observed for the W-150C and WE-150C anodes compared to samples W-50C and WE-50C. All measured microstructural features are collectively summarized in Table 2.

**Table 2.** Surface characteristics: Morphological shape, pore coverage (PC), surface roughness ( $R_s$ ) and homogeneity score ( $H_s$ ) for W-50C, W-150C, WE-50C and WE-150C.

| Features              | W-50C                | W-150C                | WE-50C               | WE-150C               |
|-----------------------|----------------------|-----------------------|----------------------|-----------------------|
| Shapes                | Hill like<br>Islands | Concave<br>hemisphere | Hill like<br>Islands | Concave<br>hemisphere |
| PC /%                 | 22.1                 | 19.2                  | 25.6                 | 20.9                  |
| $R_s$ / $\mu\text{m}$ | 0.62-0.71            | 0.42-0.50             | 0.60-0.76            | 0.35-0.37             |
| $H_s$ /-              | 0.68-0.73            | 0.83-0.87             | 0.67-0.77            | 0.86-0.88             |

From the above results, it becomes evident that the drying temperature plays a major role. This can be understood as follows: During the spray coating process, it was observed that at a lower temperature (50 °C), the evaporation is markedly slower. On the contrary, at an elevated temperature (150 °C), ink droplets evaporate almost instantly, often without any visible wetting of the surface as soon as the droplet contacts the anode support.<sup>[23]</sup> Additionally, it must be noted that when liquids are dropped on a support at temperatures higher than their boiling point, a thin layer of vapor forms that insulates the droplet and prevents it from rapidly boiling away, known as the Leidenfrost effect.<sup>[24]</sup> Therefore, as the drying temperature significantly affects the rate of evaporation, the spread of ink droplets, the wetting behavior of the ink, and the swelling of the binder, it strongly determines the particle distribution, particle connectivity and formation of particle assemblies on the substrate surface.<sup>[25]</sup> After the detailed assessment of microstructural features, the question is now how they affect macroscopic anode layer properties. This will be discussed in the next section.

## 2.3 Macroscopic properties of anode layers

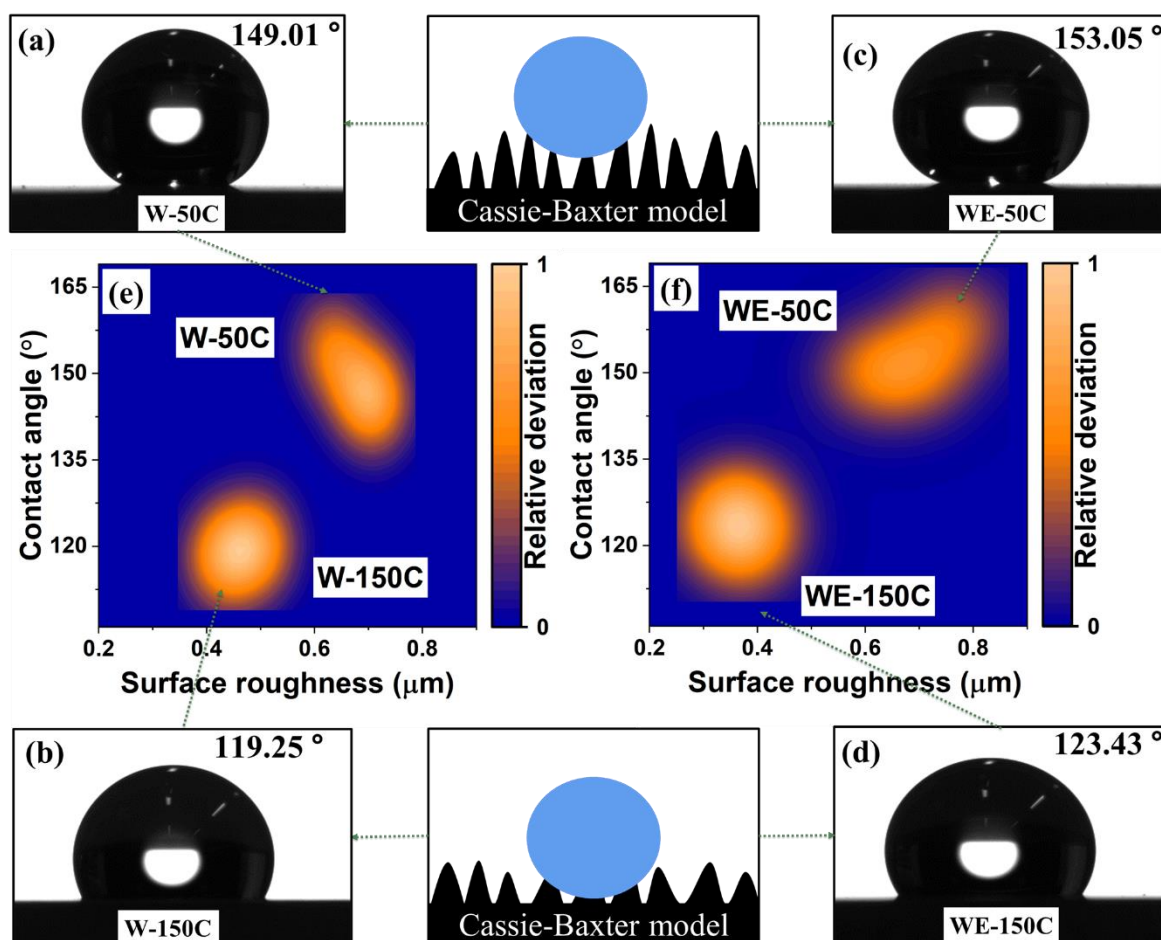
In this section, we extract macroscopic properties such as wetting as the initial interaction with the electrolyte (here: 1 M KOH) during OER and mechanical strength of the generated layers.

### 2.3.1 Wetting analysis

Wetting is a vital process that defines the mass transport mechanism during the OER. However, analyzing dynamic wetting is a complex task. In this subsection, we focused on assessing the initial wetting behavior of electrolyte on the surface of the generated layers. The contact angles measured on the four layers are depicted in Figures 5(a-d). Anodes produced at 50 °C (W-50C and WE-50C) exhibited very similar mean contact angles of  $149.01 \pm 5.18^\circ$  and  $153.05 \pm 4.80^\circ$  respectively, attributing their nearly super-lyophobic (150-180 °) nature. In contrast, anodes fabricated at 150 °C (W-150C and WE-150C) showed smaller contact angles of  $119.25 \pm 1.17^\circ$  and  $123.43 \pm 3.32^\circ$ , indicating a slight reduction in lyophobicity (90-150 °) compared to those produced at 50 °C. In this work, we utilize the terms *lyophilic* (0-90 °) and *lyophobic* (90-180 °) to describe surface-electrolyte interactions, which are comparable to *hydrophilic* and *hydrophobic* interactions when water is the contacting liquid. However, several studies have employed the terms *lyophobic* and *lyophilic* to describe interactions involving other liquids as the contacting medium.<sup>[26]</sup> Taking the standard deviation into account, the solvent composition used in the ink formulation did not significantly affect the

surface wettability. Instead, the primary factor influencing wettability is the temperature used during the coating process.

Contact angles measured from the selected regions were plotted using a 2D density plot (or kernel plot).<sup>[27]</sup> This visualization helped to understand the relationship between surface roughness and contact angles, and their distribution across the layers. Specifically, Figure 5(e-f) explore the found relationship between roughness and contact angles, where it is observed that a lower roughness corresponds to a lower contact angle, implying increased wettability on the surface. This trend is consistent in both kernel plots, and it is important to note that it is the same for both continuous phases applied in the ink formulation. This underscores the role of surface roughness in modulating surface wettability of alkaline media in addition to the chemical composition of the anode.



**Figure 5.** Static contact angle on spray-coated anodes along with wetting models: (a) W-50C, (b) W-150C, (c) WE-50C, (d) WE-150C. Relation between the surface roughness ( $R_s$ ) and contact angle ( $\theta$ ) of the layers: (e)  $R_a$  vs.  $\theta$  for water-based anodes, (f)  $R_a$  vs.  $\theta$  for water-ethanol-based anodes.

Our findings align with existing studies that apply the Cassie-Baxter model in surface-liquid interface analysis.<sup>[28]</sup> In brief, the Cassie-Baxter model describes a scenario where air pockets are trapped under the liquid, leading to the observation of increased contact angles in heterogeneous systems.

$$\cos\theta [CB] = f_s(1 + \cos\theta[flat]) - 1 \quad (1)$$

Where  $\theta[CB]$  is measured contact angle on the rough surface,  $f_s$  is solid/liquid contact area,  $\theta[flat]$  is contact angle of the flat surface with similar intrinsic material properties.

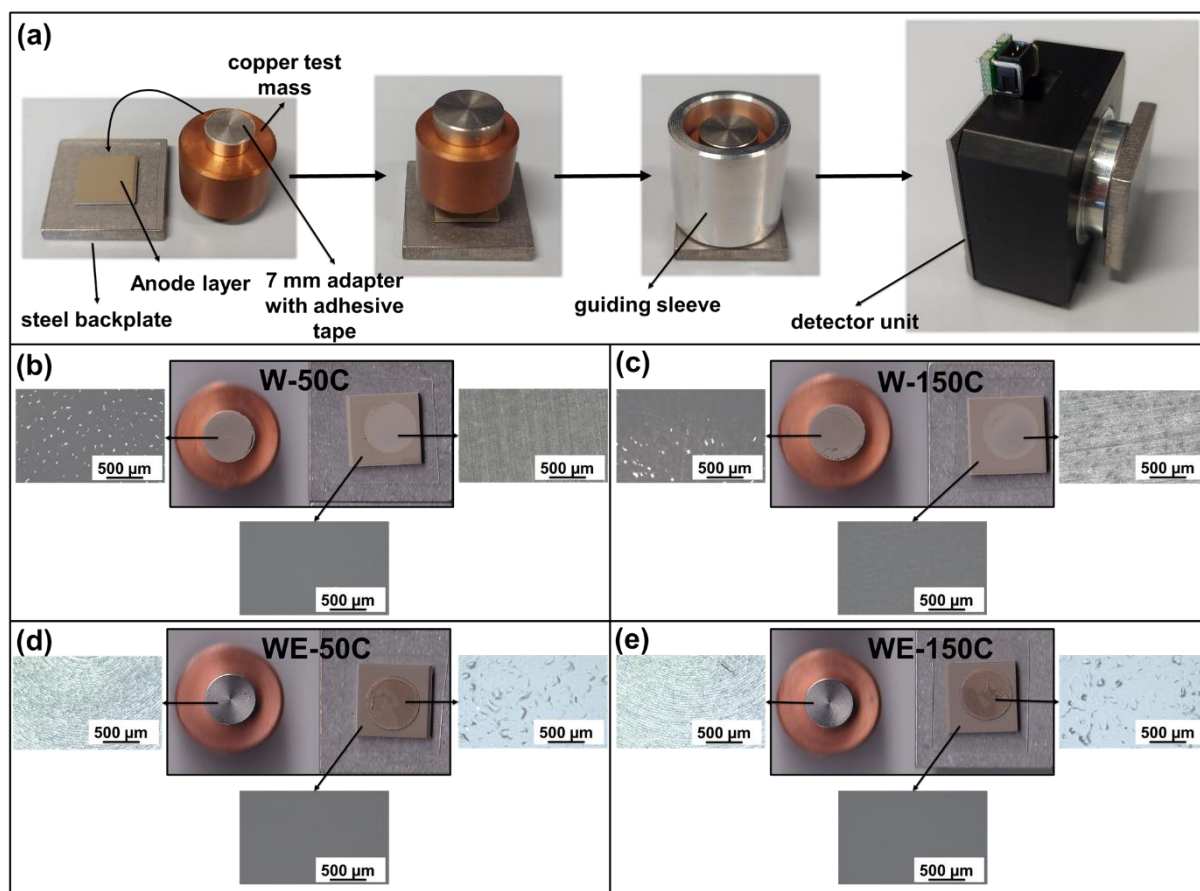
In our system, we found that the pore coverage is an effective qualitative indicator for predicting the wetting state, that could be even used quantitatively when the contact angle of the smooth surface would be known. We ascribe this to the fact that the pore coverage of the layers defines the amount of air trapped within the anode microstructure in such a way that higher pore coverage results in more air entrapment. In conclusion, the found trend in roughness and pore coverage aligns with the expected behavior when assuming the wetting behavior to follow the Cassie-Baxter model. Though not yet being frequently used in the community of water electrolysis and just described in a few studies, mostly driven by researchers focusing on porous media,<sup>[29]</sup> we believe that the Cassie-Baxter model could enable improved bubble management and the rational design of electrode surface morphology.

### 2.3.2 Adhesion analysis

A major problem with anode layers in alkaline water electrolysis is degradation and delamination over time. Despite these challenges, such sources for failure are rarely measured due to the complexity and tedious nature of the process. In this work, we utilized a commercial device for centrifugal detachment and developed a measurement routine specifically for nanoarchitected layers to evaluate the mechanical strength (see the experimental section for measurement protocols). In brief, the specimens for adhesion analysis by centrifugal detachment were assembled as shown in Figure 6a. The nickel supports with catalyst layers are bonded to a steel backplate. A copper test mass is glued on top of it with a defined adapter area. All together is inserted into a guiding sleeve and a detector. Thus, centrifugal forces can be applied orthogonal to the catalyst layer on the nickel substrate until the detector determines the breaking of the specimen. The fracture images of the fabricated layers, presented in Figure 6 (b-e), revealed distinct features: the left side of each image shows the adhesive-mounted assembly, while the right side displays the anode glued onto the measurement support. These images were captured post-measurements.



For anodes fabricated with water-based inks, the strengths at cohesive failures are  $0.77 \pm 0.10$  MPa and  $0.45 \pm 0.09$  MPa for W-50C and W-150C, respectively. This indicates the superior interfacial strength between anode support and catalyst layer compared to the inter-particle strength within the layer. However, some parts of the catalyst particles in the anode layer were detached from the anode support, as it is evidenced in micrographs that were taken after fracture-testing and that are shown in Figure 6(a-b). Additionally, adapter micrographs in Figure 6(a-b) present the holes within the layers. From this we conclude a weaker particle connectivity in terms of cohesion within the anode layer than adhesion between the particles and the nickel support. In stark contrast, anodes fabricated with a water-ethanol mixture, depicted in Figure 6(d-e), exhibit fractures at the adhesive utilized for the adherence experiments and particles indicating high mechanical strength. In comparison, anodes produced with the WE mixture show strengths of  $1.57 \pm 0.18$  MPa and  $1.28 \pm 0.23$  MPa at adhesive rupture for WE-50C and WE-150C respectively. This demonstrates stronger interparticle connectivity within the anode layer and improved interfacial strength between the anode layer and the anode support.



**Figure 6.** Adhesion analysis by centrifugal detachment. Assembly of specimens for adhesion analysis (a) with images after centrifugal detachment along with micrographs of adapter (left), layer (below), and after rupture (right): (b) W-50C, (c) W-150C, (d) WE-50C, (e) WE-150C.

For instance, taking the standard deviation into account, the drying temperatures showed negligible effect on the mechanical strength of the layers. Instead, the solvent choice in the ink formulation emerged as the dominant factor influencing the mechanical properties. Despite the still ongoing challenge in interfacial characterization of nanoarchitected layers that prevents us from making quantitative conclusions about microstructural effects on the mechanical strength, it is clear that the interaction between the continuous phase, binder, and coating process mechanisms at different drying temperatures plays a crucial role. This interplay can be further explained as follows:

1. Firstly, as noted in section 2.2.1, a stable ink, such as the Ni-Co-O particles dispersed in water-ethanol mixtures, ensures a uniform distribution of particles over the anode support, leading to increased contact area between particles within the layers. In contrast, agglomerates that form in the less-stable water-based ink spread on the support, creating weaker connectivity of particles.
2. Secondly, as mentioned in Section 2.1, the added Nafion binder can swell in the presence of alcohol,<sup>[30]</sup> further enhancing the binding strength between particles at their contact points formed during coating and drying.
3. Thirdly, as noted in the previous section, the lyophobic nature of the layers during multilayered coatings plays a significant role. Initially, the water-based coatings spread well on the Ni plate due to its lyophilic properties. However, after several layers are applied, the presence of Nafion renders the surface more lyophobic/hydrophobic, slowing down the wetting of subsequent layers and thereby reducing interparticle cohesion. This effect is minimum in case of water-ethanol based coatings.
4. Lastly, the azeotropic boiling point of the catalyst inks must be also considered as a co-solvent-effect in case of water-ethanol based coatings. Since the utilized mixture of water-ethanol (0.5:0.5) in the respective ink is lower than the azeotropic composition of water-ethanol (4.375: 95.635),<sup>[31]</sup> ethanol evaporates first, followed by water, which remains in the liquid phase. This process influences the process of layer formation,<sup>[32]</sup> thus impacting the particle connectivity.

Altogether, the measured difference highlights the prevalence of cohesive failure in anodes utilizing pure water as continuous phase and the stronger mechanical strength observed in water-ethanol-based anodes due to stronger interparticle connectivity.



This analysis of anode layer properties underscores the intricate relationship between the microstructure of the catalyst layer in terms of the pore coverage as well as the surface roughness with wettability and the mechanical properties of the coatings. All layer properties are summarized in Table 3.

**Table 3.** Anode layer properties: Measured contact angle ( $\theta$ ) and mechanical strength ( $\sigma$ ) for W-50C, W-150C, WE-50C and WE-150C.

| Properties          | W-50C           | W-150C          | WE-50C          | WE-150C         |
|---------------------|-----------------|-----------------|-----------------|-----------------|
| $\theta / ^\circ$   | 149 $\pm$ 5     | 119 $\pm$ 1     | 153 $\pm$ 4     | 123 $\pm$ 3     |
| $\sigma$ /MPa       | 0.77 $\pm$ 0.10 | 0.45 $\pm$ 0.09 | 1.57 $\pm$ 0.18 | 1.28 $\pm$ 0.23 |
| Wettability         | Super-lyophobic | Lyophobic       | Super-lyophobic | Lyophobic       |
| Mechanical failures | Cohesive        | Cohesive        | No failure      | No failure      |

The interplay between KOH and the anode surface is important and shall not be overlooked as it governs both the bubble removal and the adsorption of reactants during OER.<sup>[33]</sup> But also the requirement of mechanical stability is obvious, especially when rationalizing that interparticle connectivity and the interface between anode layer and anode support helps in avoiding contact resistance, and durability of anodes in OER.<sup>[34]</sup> However, so far only anode layer properties were quantified and hypothetically linked with electrochemical properties. Therefore, in the last chapter, we will close this gap and connect microstructure and the resulting layer properties with electrochemical performance measures.

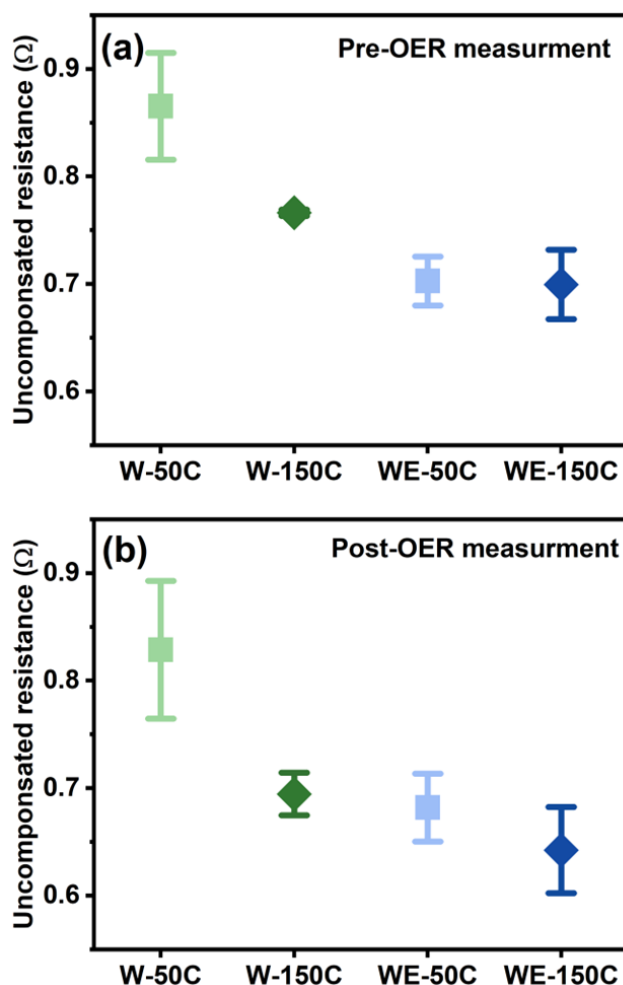
## 2.4 Electrochemical properties of anode layers

Electrochemical characterization was carried out using a 3-electrode beaker-cell setup, adjusted for plate electrodes from the work presented by Thissen et al.<sup>[35]</sup> Please see the Experimental section and supplementary information, section S4, for a detailed description of the measurement protocol.

### 2.4.1 Ionic and contact resistance within beaker cell

The uncompensated resistance ( $R_u$ ) refers to the inherent resistance within the electrochemical cell, measured when no current flows.  $R_u$  is primarily composed of ionic electrolyte resistance, as well as inter-particle contact resistances between particles and the support. Since the electrolyte and the anode support were identical for all measurements, we attribute the measured differences mainly to the particle-particle and particle-support interactions.

Figure 7(a-b) show the uncompensated contact resistance measured before and after OER. Due to the proximity of the reference electrode to the working electrode (see Experimental Section), all  $R_u$ 's are well below 1  $\Omega$ . The influence of ink composition on  $R_u$  is evident:  $R_u$  is lower for WE-50C and WE-150C compared to W-50C and W-150C, both before and after OER measurements. More notable differences in contact resistance are observed when comparing the different drying temperatures: While between W-50C and WE-50C a difference of about 150 m $\Omega$  is present, the difference between W-150C and WE-150C is only 50 m $\Omega$  and for both electrodes the  $R_u$  drops slightly after OER.



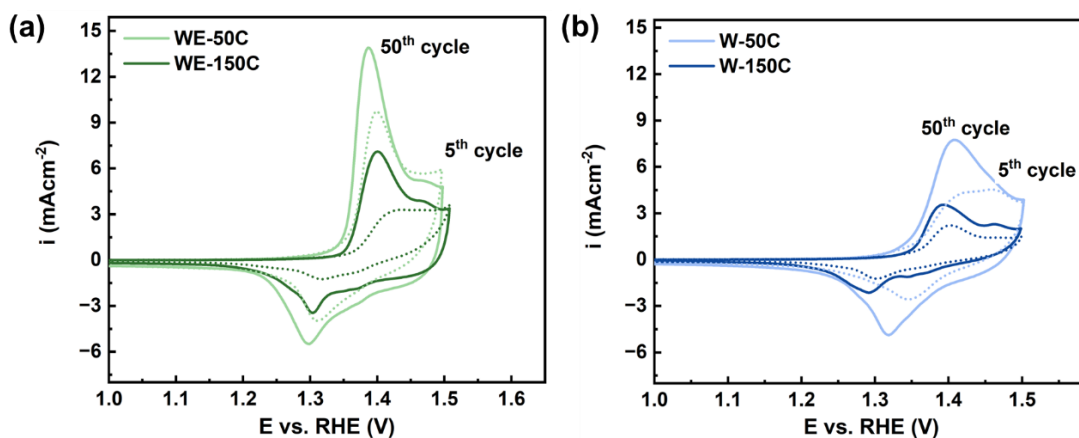
**Figure 7.** Uncompensated contact resistance ( $R_u$ ) between electrolyte, anode layer and support, measured at open circuit potential at different points of the protocol. (a) Pre-OER measurement, (b) post-OER measurement.

Particularly in the case of a microstructure with higher surface roughness and pore coverage (W-50C and WE-50C), ionic and contact resistance correlate directly with the adhesion analysis presented in the previous section. Water-based anode exhibit weaker inter-particle cohesion, leading to increased contact resistance. This suggests that the mechanical strength

of the anode layers, defined by the inter-particle connectivity, has a direct impact on the uncompensated contact resistance. However, in the case of a microstructure with lower surface roughness and pore coverage (W-150C and WE-150C), a slight dependency of the mechanical strength on uncompensated contact resistance is observed.

#### 2.4.2 Electrochemical activation by conditioning

Electrochemical conditioning is commonly applied to remove contaminants from the electrode surface and ensure reproducible starting conditions for every sample. Furthermore, it can also activate the electrode and improve its performance.<sup>[36]</sup> Here, we give a qualitative description of the process-induced surface changes by analyzing the conditioning cycles of the different electrodes. Figure 8(a-b) shows the 5<sup>th</sup> (dashed lines) and 50<sup>th</sup> (solid lines) cycles of the conditioning step. All anodes increase the surface charge passed for every cycle throughout the procedure. This is ascribed to the growth of the hydroxide layer during the phase transition from Ni(OH)<sub>2</sub> to NiOOH species at higher potentials on the catalyst surface, which essentially forms a NiOOH/CoOOH-like structure.<sup>[37]</sup> When comparing the 50 °C anodes with the 150 °C anodes as well as the W and WE based inks, a distinct difference is observed for the charge passed during the redox transitions. In general, the WE-based electrodes show larger redox-charges than those prepared with water only. Furthermore, the electrodes dried at 50 °C both show larger redox features than their 150 °C counterparts. Overall, the charge over the oxidation/reduction peak after conditioning arrange in the order, WE-50C>W-50C≥WE-150C>W-150C For all samples, we observe two (distinct) redox features. While the intensities vary, the peak positions of all anodes are similar. This indicates no differences in the present Ni-Co-O-phase, which is in line with the microstructural analysis presented in section 2.2.



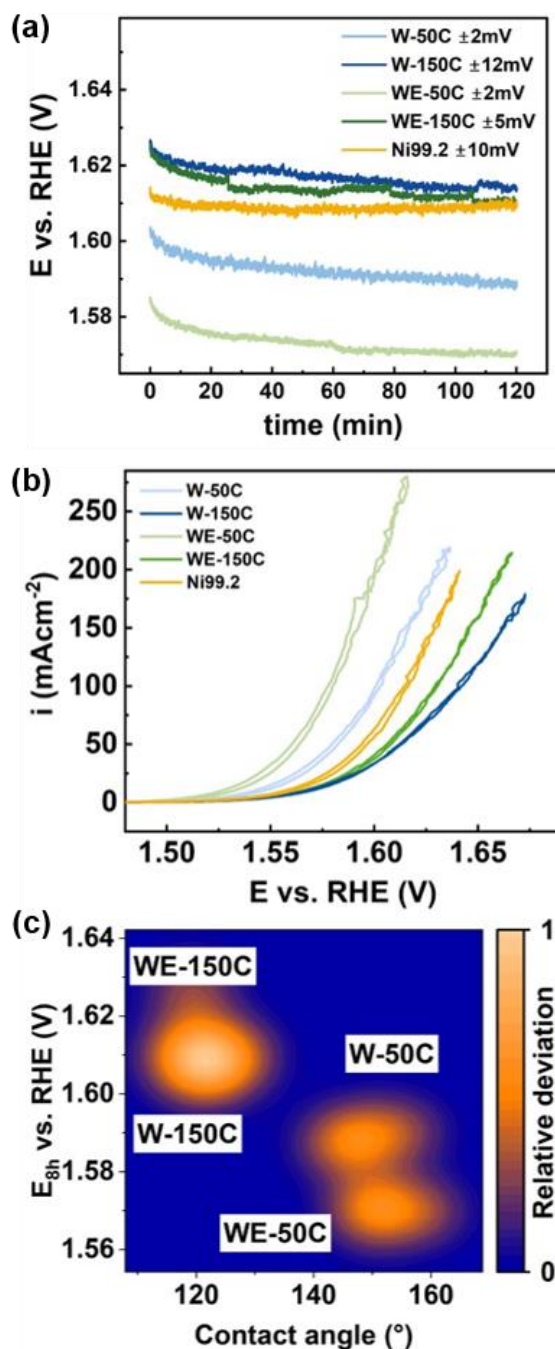
**Figure 8.** (a) Conditioning of WE-50C and WE-150C and (b) conditioning of W-50C and W-150C.

The change in passed surface charge is a qualitative indicator that the surface area for hydroxide formation has increased, or that the -OOH formation is facilitated, yielding more of the suspected OER-active  $\gamma$ - or  $\beta$ -NiOOH-phase. However, a quantitative analysis of the electrochemical active surface area is not attempted due to the mixed-metal species in Ni-Co-O, making the assignment of the charge to individual active sites impossible.

#### 2.4.3 Electrochemical activity

The activity and stability of anode layers are critical factors in determining the overall efficiency and durability of electrochemical systems, particularly in reactions like the OER. Figure 9a illustrates the behavior of the electrodes during the 2 h chronopotentiometry (CP) of the last protocol cycle as well as that of a bare Ni-support (Ni99.2). Ni itself exhibits a distinct non-porous microstructure and demonstrates excellent OER performance when exposed to iron-containing electrolytes.<sup>[38]</sup> Here, electrolytes with a constant Fe-content of 200 ppb were used and Ni is used primarily as a reference point for comparison. In total, four CPs were conducted, the corresponding graph can be found in Figure S5. Please note that the peculiar activation and deactivation behavior of the anodes in between protocol cycles is the objective of ongoing investigations. All coated electrodes show a slight activation, as the potential drops over the 2 h experiment. While W-150C and WE-150C have a higher potential at the beginning of the CP, they almost converge with the bare Ni-support towards the end. Interestingly, despite maintaining constant mass loading ( $415 \pm 30 \mu\text{m}/\text{cm}^2$ ) and similar chemical compositions (see section 2.2.2), W-50C and WE-50C exhibited superior performance relative to the Ni-support (Ni99.2), with a lower potential of about 40 mV at the end of the CP for WE-50C.

The dynamic activity measurement by cyclic voltammetry (CV) (Figure 8b) further corroborates the distinct performance differences in the anodes. The CVs reflect the activities as recorded at the beginning of the CP, though they were measured at the end of the protocol. At  $100 \text{ mA cm}^{-2}$  the potentials range from 1.578 V to 1.642 V, and the activities arrange in the order WE-50C>W-50C>Ni-support>WE-150C>W-150C. As described in section 2.4.2, this performance difference aligns well with the passed charge. This trend clearly shows that there is a correlation between the formation of active -OOH species and the activity, which we link to the surface morphology of the anodes. A second approach to validate the difference observed among the layers is given in the supplementary information section S6, where we determine the active surface area of the electrode via CV cycling



**Figure 9.** (a) Short term stability (CP at 100 mA cm $^{-2}$ ) and (b) dynamic activity (CV from 1 V to 1.8 V, 5 mV s $^{-1}$ ) of the last protocol cycle (c) kernel plots to correlate the potentials at 100 mA cm $^{-2}$  after 4x2h of stability measurements to the contact angles.

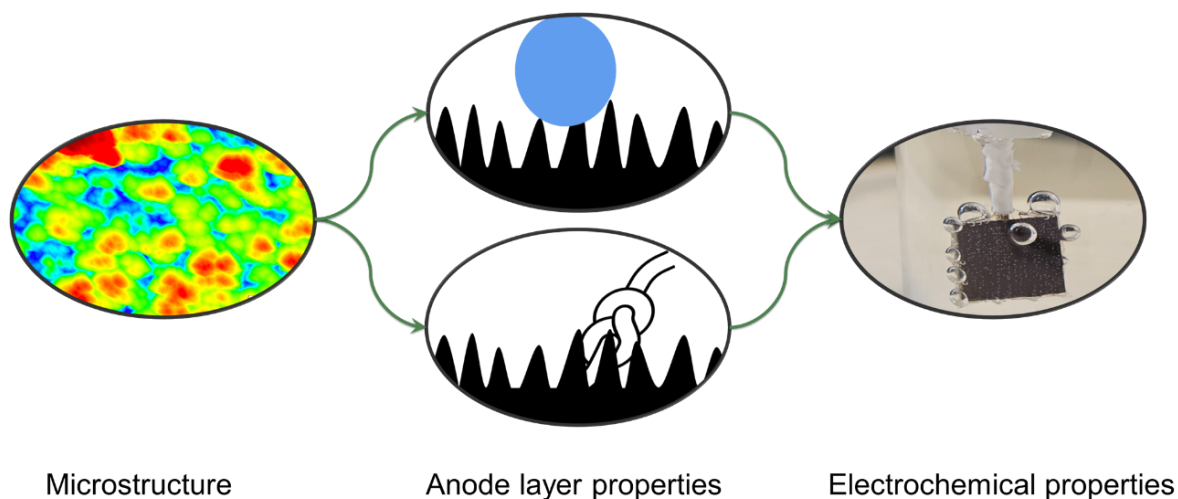
To correlate the structural analysis to the observed electrochemical performance, the contact angle measurements were correlated to the electrochemical activity after 8h OER using 2D-kernel plots. Figure 9c demonstrates that a decrease in contact angle correlates with a lower electrochemical activity, independent of the solvent compositions used in the ink formulation. It is worth considering that the surface roughness along with pore coverage are the main

driving force for the wetting behavior, highlighting the importance of the Cassie-Baxter model to describe this effect. A higher lyophilicity commonly is expected to improve the accessibility of the electrolyte to the electrode surface, and hence more accessible active sites.<sup>[39]</sup> However, the presence of oxygen bubbles creates a complex three-phase contact line during OER.

Studies on bubble detachment found out that an increase in lyophobicity, i.e., lower lyophilicity, has a direct impact on gas adhesion. Surfaces with higher lyophobicity increase the gas bubble size and facilitate the removal of gas bubbles from the surface.<sup>[40,41]</sup>

Specifically, Chang et al. demonstrated that superhydrophobic surfaces facilitate the merging of small gas bubbles into larger ones, which detach more easily due to buoyancy. The non-wetted surface creates pathways for gas flow between adherend bubbles. The spontaneous growth of larger bubbles occurs as smaller ones combine, driven by capillary pressure differences.<sup>[41]</sup>

In our case, the anodes fabricated at 50 °C exhibit higher lyophobicity, according to the previously described factors, which can effectively improve bubble transport. On the other hand, the high surface roughness in total exhibits more active sites. Among the super-lyophobic layers, the electrochemical activity is slightly lower for W-50C compared to WE-50C. This difference might be attributed to the interparticle connectivity within the layers as described in section 2.3.2.



**Figure 10.** Strategic approach for maximizing the performance of the anode layers by optimizing their macroscopic properties via the microstructure.

To sum up, in this study we fabricated four anode layers (W-50C, W-150C, WE-50C, and WE-150C) with constant composition but differing microstructure and macroscopic properties. These layers showed clear differences in electrocatalytic activity. The WE-50C

layer outperformed the other layers and was produced based on a highly stable ink. The best-performing anode layers exhibited a hill-like surface morphology with increased surface roughness causing beneficial lyophobicity. Additionally, this layer exhibited a binder-mediated improved mechanical strength that resulted in a reduced uncompensated resistance. We were able to showcase that altogether these parameters increased the electrochemical performance and how they enable a rational, knowledge-based electrode development in the future, where electrochemical target properties can be maximized by tailoring the wetting and adhesion properties via the microstructure (Figure 10).

### 3. Conclusion

In conclusion, we demonstrated the effect of anode layer microstructure as a proof-of-principle for achieving efficient OER. For this investigation, we employed two different solvent compositions and two distinct drying temperatures. Subsequently, the microstructure and macroscopic properties of the anodes were identified and quantified. These properties are correlated to electrocatalytic activity and stability.

We found that the solvent composition has a more significant impact on the stability of catalyst inks and the mechanical strength of the anode layers, while the drying temperature predominantly influences surface features and wettability. At 50 °C, slower evaporation leads to the formation of islands and a highly porous microstructure, along with increased surface roughness, thereby enhancing lyophobicity. Conversely, at 150 °C, rapid evaporation results in the formation of concave, hemisphere-shaped structures with lower pore coverage and reduced surface roughness, leading to decreased lyophobicity. Anode layers with increased microstructure-mediated lyophobicity exhibited enhanced electrochemical performance by increasing the amount of available active sites and facilitating effective bubble transport. Moreover, at lower drying temperatures, the resulting higher mechanical adherence, characterized by stronger particle connectivity, reduced the uncompensated contact resistance within the beaker cell.

Taken together, our study revealed that by optimizing the anode layer of a given material via its microstructure towards the unravelled wetting and adhesion properties, we can effectively transport bubbles, expose more active sites and reduce contact resistance. These adjustments are pivotal parameters that must be carefully considered in the design and development of highly active and stable engineered anode layers for alkaline water electrolysis using nano-sized metal oxides.

## 4. Experimental Section/Methods

### *Ink preparation*

Commercial nickel cobalt oxide nanoparticles ( $\geq 99.9999\%$ ) were sourced from Sigma-Aldrich. Deionized (DI) water, with a resistance exceeding  $18.1\text{ M}\Omega$ , was obtained from a Milli-Q system. Nafion™ perfluorosulfonic acid (PFSA) 5% dispersion (D521) was acquired from Ion Power GmbH and integrated into the ink formulation without further modification. Two formulations were prepared: one using pure Milli-Q water and the other a mixture of Milli-Q water and analytical grade isopropanol as carrier liquids. The binder-to-catalyst ratio was maintained at 0.2, and the total solid concentration was set to  $1\text{ mg/ml}$ . Initially, the catalyst was mixed with the selected carrier liquids. A tip Sonicator (Branson SFX550) dispersed the components for 12 minutes at an amplitude of 20 %, operating in pulse mode with 1-second intervals of sonication and rest. Subsequently, Nafion was added, and the mixture was further sonicated for 6 minutes under the same conditions. An ice bath was employed to prevent the ink from overheating and re-agglomeration. Sonotrode heating characteristics are added in Figure S1c.

### *Ink characterization*

All inks were characterized by utilizing analytical centrifugation (Analytical Centrifuge LUMisizer 6514–44, LUM GmbH). Samples of  $410\text{ }\mu\text{L}$  were filled into polycarbonate (PC) tubes and placed inside the centrifuge. All measurements were conducted at 2500 RPM and  $20\text{ }^{\circ}\text{C}$ . The captured fingerprints were then converted into transmittograms for improved understanding and comparison.

### *Layer fabrication*

The inks were deposited onto nickel plates (99.2%, HMW Hauner,  $1\text{ cm}^2$  projected area) using an ultrasonic spray coater (Sono-Tek Co., NY). Prior to coating, the nickel plates were cleaned through a chemical etching process in a  $1\text{ M HCl}$  solution for 5 minutes, followed by rinsing with acetone and then isopropanol, each for 5 minutes, in a sonication bath (Elmasonic S 30 H, Germany) at ambient temperature. The inks were applied at a constant flow rate of  $0.4\text{ ml/min}$ , with a total of 80 layers being deposited. For uniform coating, the initial layer was sprayed horizontally across the plate. Subsequently, the spray direction was adjusted by 90 degrees, and the next layer was applied perpendicularly to the previous one. This alternating pattern continued until all 80 layers were completed. The final mass loading was



assessed using a precision balance by using the A&D BM-22 microbalance, with the coatings achieving the loadings of approximately  $415 \pm 34 \mu\text{m}/\text{cm}^2$ .

### *Layer characterization*

Morphological analysis was conducted using SAM-EDX with a Scanning Auger Nanoprobe 710 of the company Ulvac-Phi, equipped with an EDAX Octane Elite detector for energy-dispersive X-ray spectroscopy (EDX) analysis. Surface topography measurements were obtained through atomic force microscopy (AFM, TOSCA 400, Anton Paar Germany GmbH) using in-house-developed MSDQ. The methodologies and conditions applied in this study were consistent with those detailed in our previous work<sup>[22]</sup> and parameters utilized are summarized in supporting information, section S3.

For determination of pore coverage, the anode layer on Ni plate was mounted on a SEM sample holder using copper tape. A Helios NanoLab 600i SEM with a focused ion beam (FIB) was employed for cross-section imaging. A protective platinum line ( $15 \mu\text{m} \times 0.5 \mu\text{m}$ ,  $0.5 \mu\text{m}$  thick) was deposited to shield the structure from high-energy FIBs. A rectangular area ( $15 \mu\text{m} \times 15 \mu\text{m}$ ) adjacent to the platinum line was selected, and a  $5 \mu\text{m}$  deep hole was created using a  $6.5 \text{ nA}$  FIB beam current. The undamaged wall beneath the platinum deposition was polished with lower current ion beams (up to  $93 \text{ pA}$ ) to obtain a smooth cross-section. Finally, images at various resolutions were captured using the SEM. The images obtained from the FIB-SEM device were processed using a MATLAB R2022a algorithm. The algorithm enhances image contrast to distinguish catalyst particles from pores, then binarizes the images into black (catalyst) and white (pores) pixels. Porosity is calculated by determining the ratio of white pixels (pore area) to the total pixels, representing pore coverage of the anode layer.

To quantify the adherence and coherence of the coatings under tensile stress, the centrifugal adhesion analyzer LUMiFrac<sup>®</sup> from the company LUM has been employed. For this method, the samples have to be prepared appropriately. First, the catalyst coated nickel substrate was glued to a stainless steel backplate and on the top of the anode layer a copper test mass with a round adapter of  $10 \text{ mm}$  diameter is placed using an acrylic adhesive tape with a PET backbone (Lohmann DuploCOLL 362.2). Thus, the sample was in between the backplate and the test mass. In the second step, the specimen was placed in tight clamps for  $24 \text{ h}$  at room temperature to ensure that the pressure sensitive adhesive was at its peak strength. Finally, the specimen was inserted into an aluminum guiding sleeve, such that the copper test mass is always at a  $90^\circ$  angle to the backplate and the nickel substrate. This assembly was placed into

a detector on a centrifugal plate. The detector identified the frequency of rotation, at which the copper test mass breaks off from the coating. From this, the adherence has been calculated. Contact Angle Measurements were performed using OCA15PRO equipment (Data Physics Instruments GmbH). The measurements were conducted with 1 M KOH as the liquid which was dropped at a drop-eject-rate of  $5\mu\text{L s}^{-1}$ .

XPS measurements were performed on two Ni-Co-O films (WE-50C, and WE-150C).

Measurements were carried out using a near ambient pressure XPS equipped with an Al-K $\alpha$  source that produces monochromated X-rays of energy 1486.6 eV. After recording the survey scans using a pass energy of 100 eV, high resolution scans of all desired elements such as Ni, Co, O, C, and F were recorded applying a pass energy of 20 eV and a resolution of 0.05 eV. Data analysis was performed using the CasaXPS software.

Raman analysis was conducted on all Ni-Co-O films using a DXR Raman microscope from Thermo Scientific. An excitation line of 532 nm, and laser power of 1 mW was employed to collect the spectra.

Post-mortem SEM-EDX analysis was performed using a Hitachi Tabletop TM3030 scanning electron microscope, equipped with a Quantax70 detector for energy-dispersive X-ray spectroscopy. All samples were measured with a 15 kV accelerating voltage in the large current mode.

For EDX-analysis, we measured three arbitrary points on each sample. All data is given in normalized weight percent, whereas elements known to be introduced due to the electrochemical measurement procedure, i.e. potassium, were excluded from the datasets.

The Fourier Transform Infrared (FTIR) spectroscopy analysis was conducted to investigate the functional groups and chemical bonding in the anode coatings. FTIR spectra were recorded using FTIR spectrometer (Bruker, Vertex 80). The instrument was equipped with an RT-DLaTGS (Room Temperature Deuterated L-Alanine doped TriGlycine Sulphate) detector and a KBr beam splitter. The transmittance spectra were collected in the range of 4000–200  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The measurements were conducted at room temperature under nitrogen atmosphere to prevent any contamination from moisture and CO<sub>2</sub> interference. Each spectrum was obtained by averaging 32 scans on three different spots for each sample to improve the signal-to-noise ratio and reproducibility. The obtained spectra were then subjected to baseline correction using Bruker OPUS to enhance the clarity and accuracy of the peaks.

### *Electrochemical characterization*

The fabricated layers were employed as working electrodes (WE) in a three-electrode beaker cell setup. The setup is a modified version of the cell presented by Thissen et al., also making it applicable for plate electrodes.<sup>[35]</sup> For this, a nickel rod (99.5% trace metal base, HMW Hauner) with a 1 mm groove was employed as a current collector for the WEs.

Mercury/mercury oxide (Hg/HgO, ALS Japan) and a fine mesh (De Nora) were employed as reference and counter electrodes, respectively. The former's potential was regularly tracked vs. a true RHE<sup>[42]</sup>. 200 ml of 1 M KOH (TH Geyer) was employed as electrolyte, whereas iron (diluted in HNO<sub>3</sub>, Agilent) was added to reach a controlled concentration of 200 ppb for every batch. No stirring was applied during the measurements.

Gamry Interfaces 1010E and Ref3000 were employed as potentiostats/galvanostats equipped with Gamry Framework Data Acquisition Software Version 7 for controlling the electrochemical measurements. The same electrochemical protocol was employed for every sample, consisting of eight main steps will be briefly discussed here. A detailed description of the protocol is found in the supplementary information, section S4.

The protocol starts with the conditioning of the electrodes by cycling the potential 50 times from 0.25-1.5 V vs. RHE. This step is followed by determining the electrochemical active surface area (ECSA), by applying rapid CV cycling with increasing scan rates (5, 10, 25, 50, 100, 200, 400, 800 mVs<sup>-1</sup>, 5 cycles each). To assess the activity and stability change of the samples, four repetitions of the following three protocol steps were applied. First, the dynamic activity of the samples is measured by cycling the potential between 1-1.8 V vs. RHE three times ("Activity") followed by stationary polarization (SP) of the electrodes. For the SP, the current was measured for 180 s at consecutive potentials of 1, 1.1, 1.2, 1.3, 1.4, 1.45, 1.5, 1.55, 1.6, 1.65, 1.7, 1.75 and 1.8 V vs. RHE. The final step in the cycles consisted of a 2 h chronopotentiometric (CP) measurement at 100 mAcm<sup>-2</sup> ("Stability"). After the final cycle, the ECSA is determined with the same procedure as explained above. Before every protocol step, the uncompensated resistance ( $R_u$ ) was determined via potentiostatic electrochemical impedance spectroscopy (PEIS) at open circuit potential (AC voltage 10 mV rms, 300000 Hz-1000 Hz, 10 points per decade). The  $R_u$  was determined at the lowest absolute difference from the PEIS-phase from zero. All protocol steps were corrected with 100 % of their respective  $R_u$  value.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

AJ appreciates the International Max Planck Research School (IMPRS) Recharge graduation school for support. Authors acknowledge the financial support from the Federal Ministry of Education and Research (PrometH2eus project in the framework of H<sub>2</sub>Giga, funding number 03HY105F). DS thankful for support by the Mercator Research Center Ruhr (MERCUR.Exzellenz, 'DIMENSION' Ex-2021-0034), LG thank Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – IRTG 2803 – 461605777 for the financial support, VV thank university of Duisburg-Essen for Postdoc Seed Funding and Open Access funding enabled and organized by Projekt DEAL.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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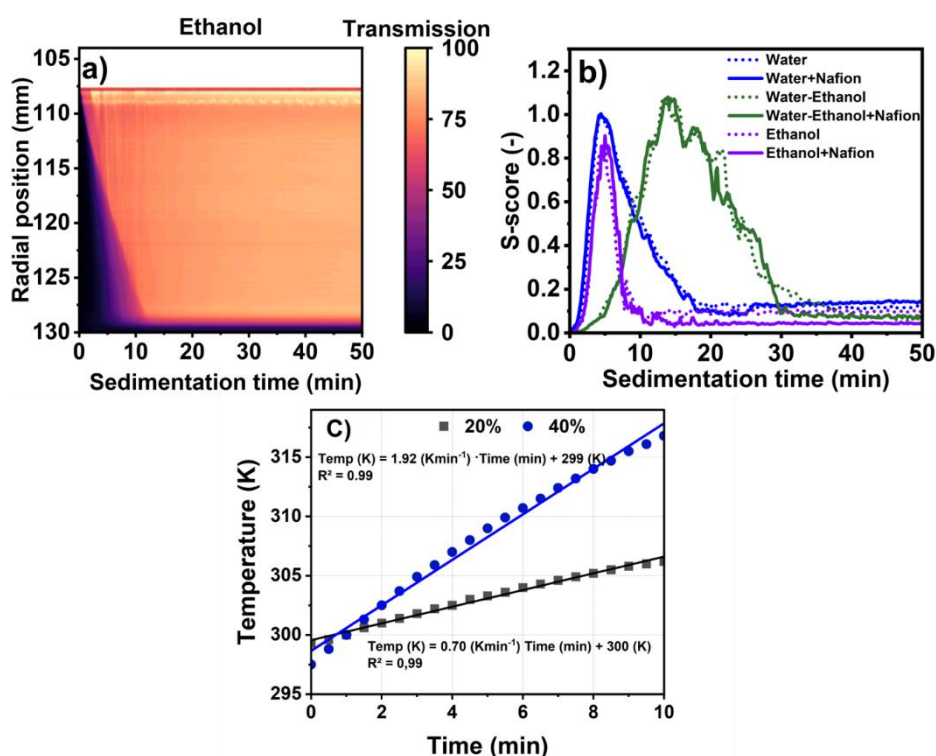
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## Supporting Information

### A Proof-of-Principle Demonstration: Exploring the Effect of Anode Layer Microstructure on the Alkaline Oxygen Evolution Reaction

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#### S1. Ink formulation



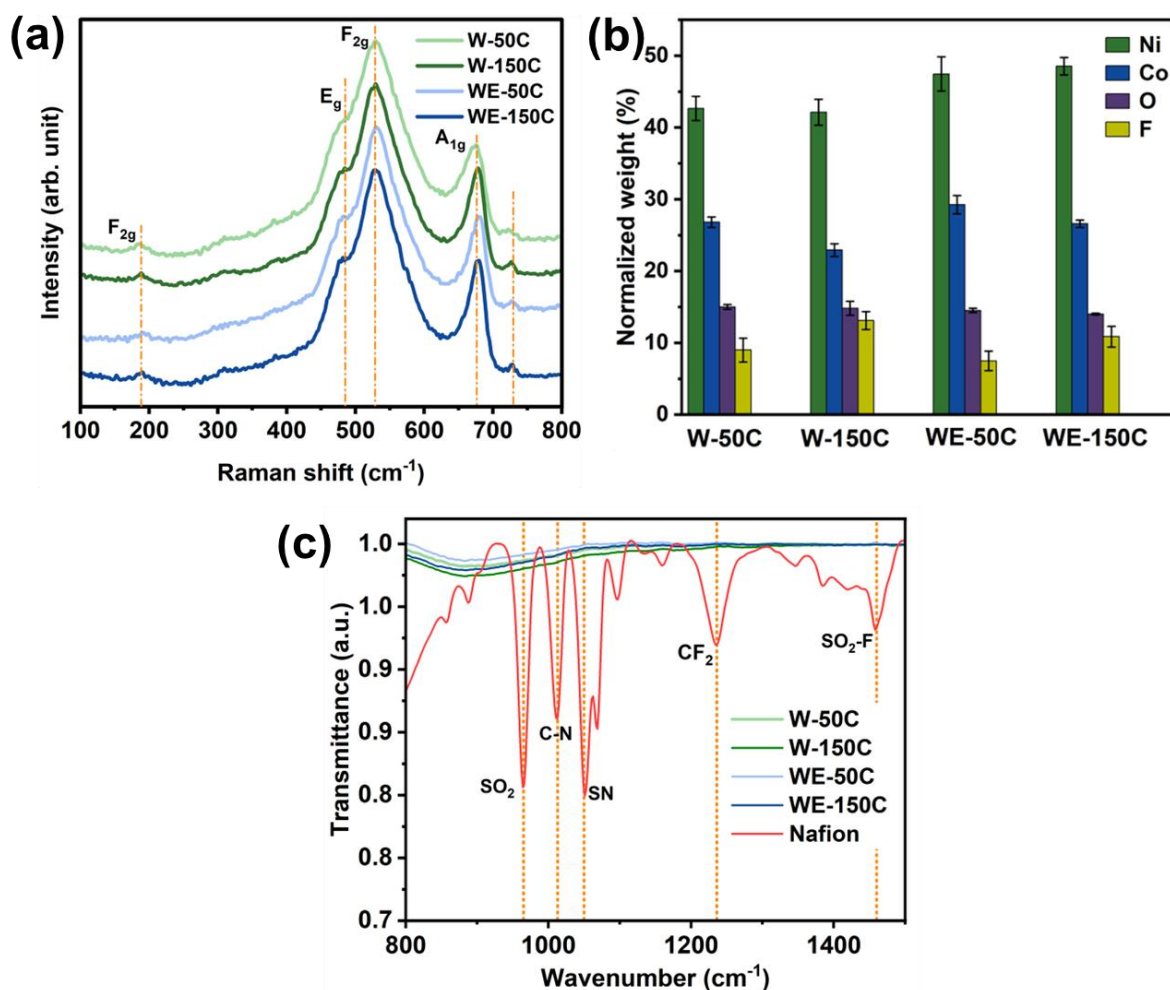
**Figure S1.** Direct visualization of time-resolved sedimentation process via transmittogram: (a) Ink prepared using ethanol as a solvent. (b) Stability trajectory of before Nafion addition and after Nafion addition. (C) Heating curves at 20 % and 70 % amplitude of the Branson sonicator with the 3 mm microtip.

#### S2. Chemical analysis

Figure S2a shows the Raman spectra of the nickel-cobalt oxide (Ni-Co-O) films which were first analyzed to evaluate their vibrational properties and any change in the electronic structure due to the different processing conditions used. All Ni-Co-O films exhibited five Raman bands at approximately 189, 480, 530, 680, and 726  $\text{cm}^{-1}$ . For nickel cobaltite powder,

Raman bands at 185, 461, 507, and 656  $\text{cm}^{-1}$  are reported corresponding to  $F_{2g}$ ,  $E_{1g}$ ,  $F_{2g}$ , and  $A_{1g}$  vibrational modes.<sup>[1]</sup> Even though an accurate assignment of the observed Raman peaks in the films based on the reported bands for nickel cobaltite is difficult, the blue shift of Raman bands in the films might indicate a more stressed lattice in the films compared to the bulk powder. In addition, the appearance of an additional peak at 726  $\text{cm}^{-1}$  also suggests the presence of a NiO phase in the deposited films, however the observed spectra do not fully resemble the Raman spectrum of pure NiO alone.<sup>[2]</sup> Importantly, when comparing the differently processed Ni-Co-O films, no significant changes were observed in the Raman spectra. This indicates that variations in the solvent matrix or drying temperature have no major impact on the electronic structure of these films.

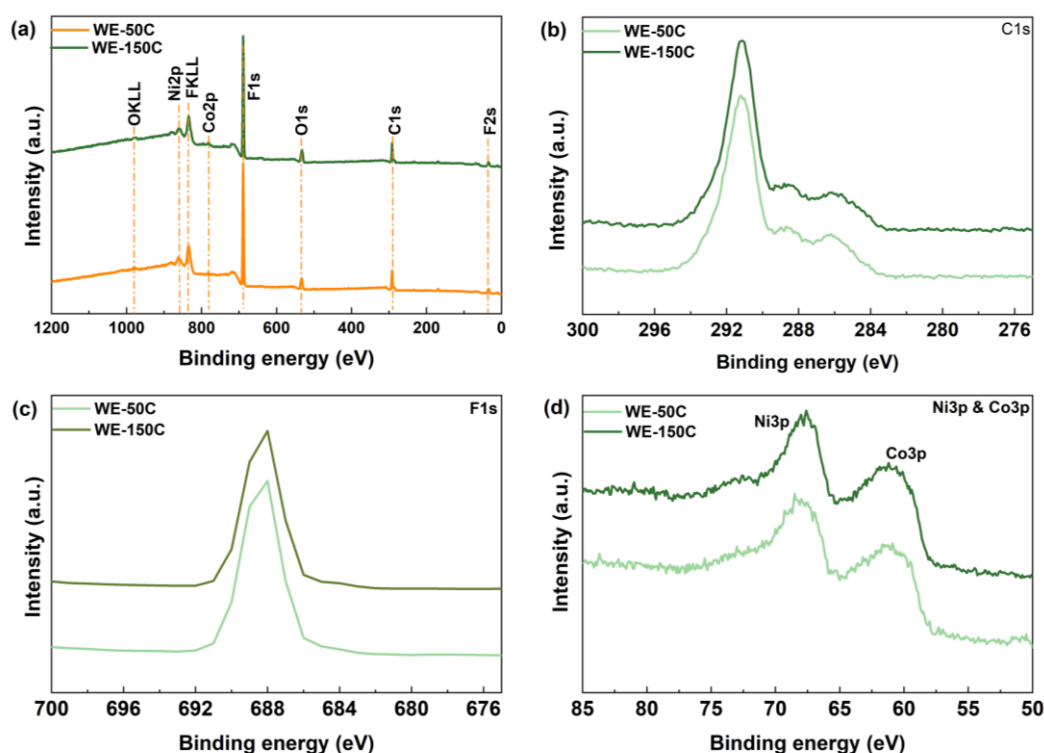
Elemental analysis (Figure S2b) of these anodes adds up to these findings. In brief, there are below 8 % elemental weight differences between the anodes when considering the elements Ni, Co, O, and F across all fabricated layers, however always a higher amount of Ni is detected over Co.



**Figure S2.** Chemical analysis: (a) Raman analysis (b) EDX elemental analysis (c) FTIR measurements.



Additionally, The FTIR spectrum of Nafion binder solution (Figure S2c) displayed several distinct peaks corresponding to its functional groups. The sulfonic acid ( $-\text{SO}_3\text{H}$ ) groups, exhibit a characteristic peak around  $1050\text{ cm}^{-1}$ , attributable to the symmetric stretching vibration of the  $-\text{SO}_3$  group. Additionally, the C–F stretching vibrations, indicative of the Teflon backbone, manifest prominently at approximately  $1150\text{ cm}^{-1}$  and  $1210\text{ cm}^{-1}$ . The region around  $970\text{ cm}^{-1}$  is often associated with the C–O–C stretching of the ether groups present in the ionomer. Moreover, the presence of water in hydrated Nafion was identified by the broad peak around  $3400\text{ cm}^{-1}$ , corresponding to the O–H stretching vibrations.<sup>[3]</sup> Comparing Nafion binder in anodes and the Nafion binder solution revealed no visible peaks in the anodes, unlike the distinct peaks present in the Nafion solution, likely due to the small amount of Nafion incorporated. Notably, comparisons among the anodes showed no significant changes.



**Figure S3.** XPS analysis of WE-50 and WE-150 films. (a) Survey spectra and high-resolution scans of (b) C1s (c) F1s and (d) Ni and Co 3p.

To further analyze the surface chemical composition with respect to different processing temperatures, we analyzed the WE-50C and WE-150C films by XPS (Figure S3). On the surfaces of both samples, the elements from the binder were detected with much higher intensities compared to the Ni and Co due to an expected coverage of the Ni-Co-O powder by the binder (Figure S3a). Chemical stability of Nafion at these temperatures was evaluated by

analyzing the high resolution C1s and F1s spectra (Figure S3b-S3c) in these Ni-Co-O films. The high resolution C1s spectrum in WE-50C shows a maximum binding energy around 291.8 eV corresponding to CF<sub>2</sub> in Nafion.<sup>[4]</sup> In agreement with this, the binding energy of F1s is located around 688.9 eV showing a clear shift from elemental F (685 eV). It is worth noting that the C1s and F1s spectra of the WE-50 sample resemble that of the WE-150 film thus underlining no significant chemical change in Nafion due to an increase in the processing temperature of these films from 50 °C to 150 °C. Unfortunately, the Ni2p region could not be considered for an in-depth analysis of the surface metal-oxide quantification due to interference from the F KLL auger peak in this binding energy region. Hence, the Ni3p and Co3p regions were subsequently analyzed (Figure S3d). As evidenced by the similar high resolution of Ni3p and Co3p spectra in both WE-50C and WE-150C films, the processing temperature does not seem to influence the surface chemical nature of oxides in these films. Overall, the XPS analysis also confirm that within the given range, the substrate temperature during spray deposition has no significant impact on the surface chemical states of these Ni-Co-O films and agrees well with previously discussed Raman results.

### S3. Multistage data quantification (MSDQ)

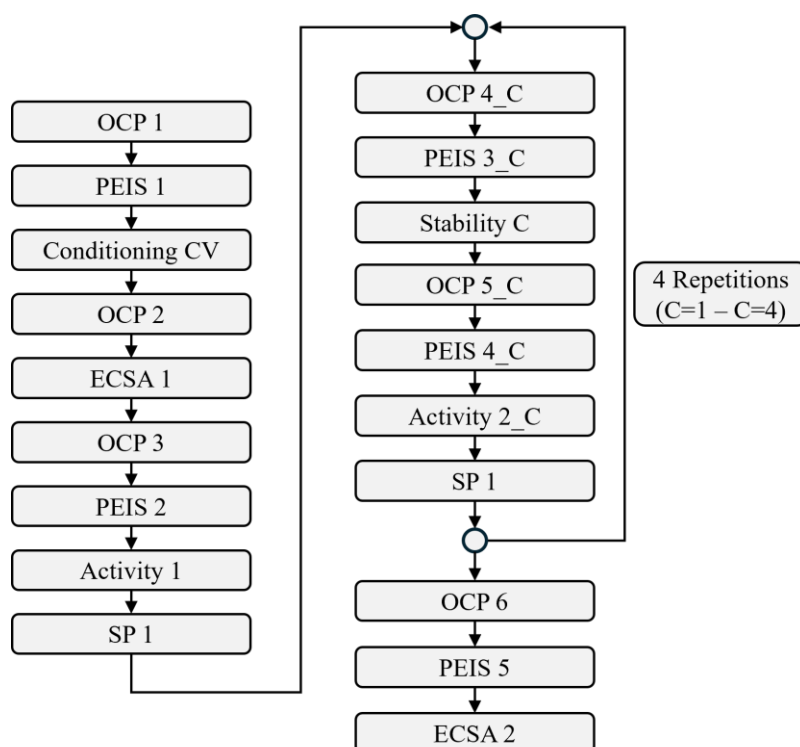
MSDQ framework was utilized to understand the quality of coatings in nanoscale within the anode surface. In brief, MSDQ is a statistical approach which involves calculation of optimal number of regions of selection (ROS) measurements, followed by distribution of these ROS fairly and equally based on the periphery rule and eventually extract the surface features. The parameters utilized in MSDQ were summarized in Table S1.

**Table S1.** Parameters utilized in MSDQ: Homogeneity score ( $H_s$ ) at different region of selection (ROS), standard deviation ( $\sigma$ ), margin of error (E), confidence interval ( $\alpha$ ) and optimal number of ROS (x) for W-50C, W-150C, WE-50C and WE-150C anodes.

| Parameters                   | W-50C | W-150C | WE-50C | WE-150C |
|------------------------------|-------|--------|--------|---------|
| $H_s$ (ROS <sub>1</sub> ) /- | 0.722 | 0.852  | 0.724  | 0.876   |
| $H_s$ (ROS <sub>2</sub> ) /- | 0.735 | 0.860  | 0.677  | 0.872   |
| $H_s$ (ROS <sub>3</sub> ) /- | 0.774 | 0.872  | 0.681  | 0.864   |
| $H_s$ (ROS <sub>4</sub> ) /- | 0.682 | 0.858  | 0.742  | 0.885   |
| $\sigma$ /-                  | 0.037 | 0.008  | 0.032  | 0.009   |
| E /%                         | 2.5   | 2.5    | 2.5    | 2.5     |
| $\alpha$ /%                  | 95    | 95     | 95     | 95      |
| x /-                         | 13    | 4      | 11     | 4       |

#### S4. Detailed electrochemical protocol

Figure S4 displays the flow sheet of the detailed electrochemical protocol. Table S2 explains the settings for the individual protocol steps.

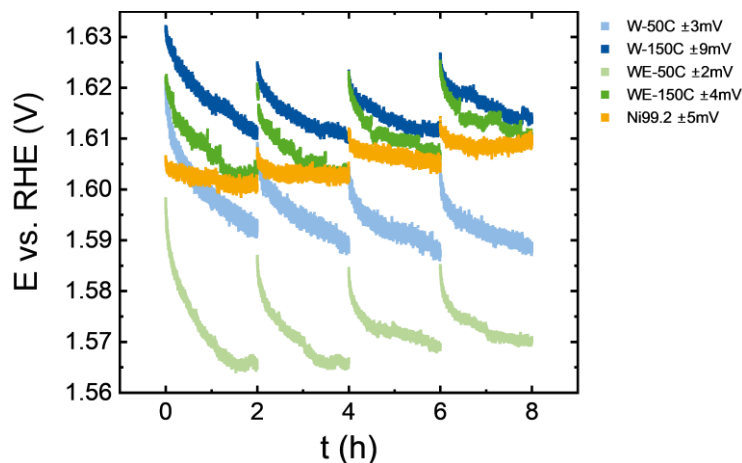


**Figure S4.** Detailed electrochemical protocol. The specific values for every step are displayed in Table S2.

**Table S2.** Protocol settings for the single steps of the electrochemical protocol, as displayed in Figure S4.

| Protocol step             | Specifications                                                                                                                                                                                                                                                                                                   |
|---------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| OCP 1 – OCP 7             | 180s                                                                                                                                                                                                                                                                                                             |
| PEIS 1 – PEIS 5           | DC voltage: preceding OCP value, AC voltage: 10 mV rms, 300000 Hz-1000 Hz, 10 points per decade                                                                                                                                                                                                                  |
| Conditioning CV           | 0.25 V – 1.5 V vs. RHE, 100 mV s <sup>-1</sup> , 50 cycles                                                                                                                                                                                                                                                       |
| ECSA 1 – ECSA 2           | 0.95 V – 0.85 V vs. RHE, 5 mV s <sup>-1</sup> , 10 mV s <sup>-1</sup> , 25 mV s <sup>-1</sup> , 50 mV s <sup>-1</sup> , 100 mV s <sup>-1</sup> , 200 mV s <sup>-1</sup> , 400 mV s <sup>-1</sup> , 800 mV s <sup>-1</sup> , 5 cycles, 20 s equilibration time at 0.95 V before the first scan of a new scan rate |
| Activity 1 – Activity 2_4 | 1 V – 1.8 V vs. RHE, 5 mV s <sup>-1</sup> , 3 cycles                                                                                                                                                                                                                                                             |
| SP 1 – SP 2_4             | 1 V, 1.1 V, 1.2 V, 1.3 V, 1.4 V, 1.45 V, 1.5 V, 1.55 V, 1.6 V, 1.65 V, 1.7 V, 1.75 V and 1.8 V vs. RHE, 180 s each                                                                                                                                                                                               |
| Stability 1 – Stability 4 | Chronopotentiometry at 100 mA cm <sup>-2</sup> , 2 h                                                                                                                                                                                                                                                             |

## S5. Full CP data



**Figure S5.** 4x2h CP at  $100 \text{ mA cm}^{-2}$  of the prepared anodes and support material. The jumps at two, four and six hours indicate the breaks in the cycle where the dynamic activity was determined.

## S6. Evaluation of the ECSA determination

The analysis of the redox transition charge has been adopted to calculate the ECSA elsewhere, however, this comes with other drawbacks such as a volume expansion during the NiOOH growth, effectively reducing the real surface area.<sup>[5]</sup> More importantly, the species formed during the observed redox-transition might be different from the active species in the OER-potential region, which is why we refrain from applying this method here.

Additional to the qualitative description of the Ni-redox features, the surface areas of the samples were estimated by measuring the electrochemical capacitance of multiple voltograms in the double-layer regime. For this, the potential was cycled as indicated in Table S3, and the positive and negative capacitance current were obtained at 0.9 V for the last cycle of the respective scan rates. The obtained current data points were plotted over the scan rate and the resulting plot fitted. The double layer capacity is then derived from the slope of the resulting linear fit, considering the relationship shown in equation S01:<sup>[6]</sup>

$$i = C_{DL} \frac{dU}{dt}, \quad (\text{S1})$$

with  $C_{DL}$  as the double layer capacitance and  $U$  as potential.

The double layer capacitance was not further normalized on a specific capacitance to obtain a geometrical value, due to the difficulties in synthesizing a single atomistic layer of catalyst.

Reports of the specific capacity state values ranging between  $C_s = 0.022\text{-}0.130 \text{ mF cm}^{-2}$ .<sup>[7]</sup>

Hence, we take the double layer capacitance as an indicator for the ECSA directly. All

capacitive values for the investigated samples, as well as for the Ni99.2 support, are displayed in Table S2. When comparing all capacitive values within either ECSA 1 or ECSA 2, no trend is visible, especially no trend which aligns with the observed activity changes of the samples. This, however, does not necessarily mean that the true active surface area of the samples in the OER active region is following the capacitive values obtained here, since the surface of the samples will change with increasing potentials. At higher oxidative potentials, hydroxide or oxyhydroxide layers might form, and thus, influence the ECSA. A detailed study on the influence of the potential region on the capacity determination would need to be done, in order to elaborate on the surface changes at OER-closer potentials.<sup>[8]</sup> Here, we can merely show, that the capacitance obtained at the specific potential of 0.9 V vs. RHE can not be linked to any activity or morphological feature of the samples.

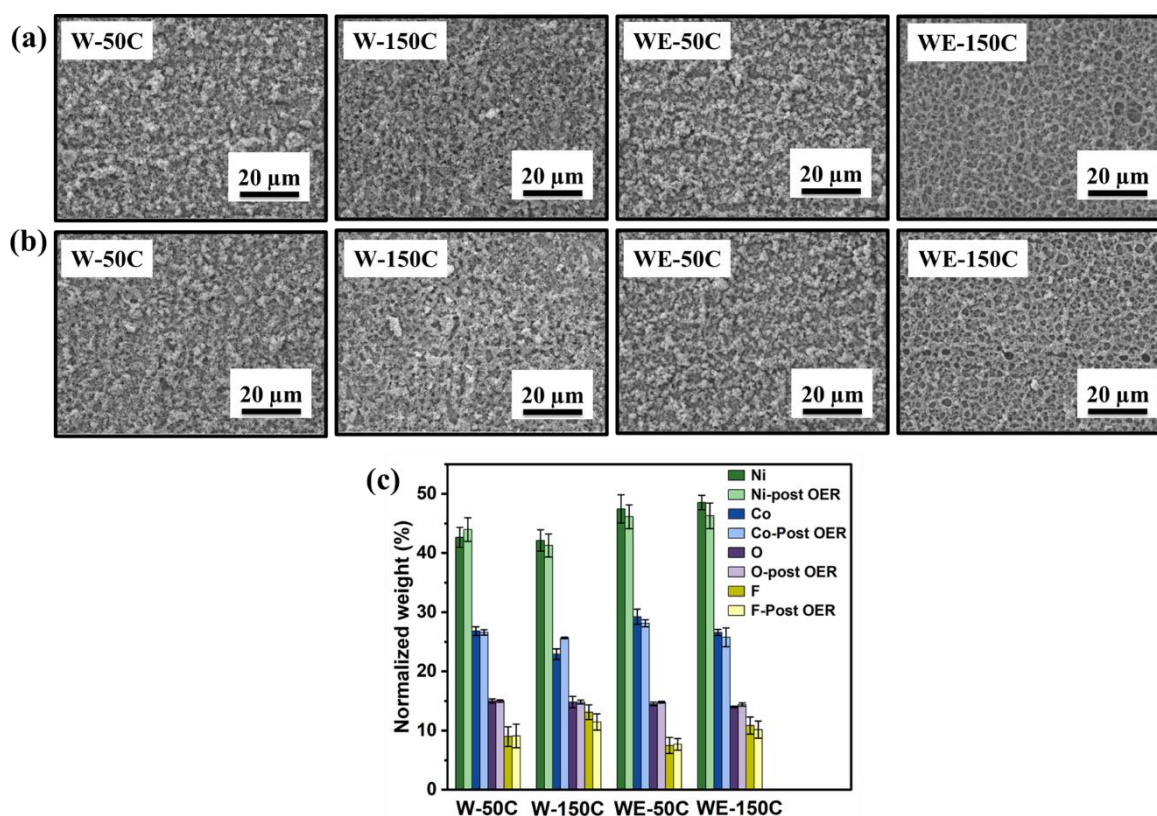
We observe a constant increase of the coated samples capacitance from ECSA 1 to ECSA 2. It amounts to  $17.5 \pm 0.2$  % and  $19.3 \pm 0.8$  % for the oxidative and reductive sweep, respectively. The nickel support material shows the highest capacitive increase of 24 % and 25 % for oxidative and reductive sweep, respectively. This increase might be explained by the continuous growth of the (oxy-)hydroxide layer during the repetitive CP steps in the electrochemical protocol. This increase in (oxy)hydroxide on the surface leads to an increase in conductivity, thereby increasing the measured capacitance. This agrees well with the decrease in  $R_u$  throughout the protocol for all samples.

**Table S3.** Double layer charging capacity determined by rapid CV cycling for the oxidative sweep ( $C_{DL,ox}$ ), and the reductive sweep ( $C_{DL,red}$ ) with their respective standard deviations (Std). Please note, that the W-150C sample only shows a single value, due to a measurement error in the data acquisition of the other two replicas.

|               | Sample  | $C_{DL,ox}$ [mF] | Std [mF] | $C_{DL,red}$ [mF] | Std [mF] |
|---------------|---------|------------------|----------|-------------------|----------|
| <b>ECSA 1</b> | W-50C   | 0.124            | 0.005    | -0.128            | 0.005    |
|               | W-150C  | 0.135            | --       | -0.138            | --       |
|               | WE-50C  | 0.128            | 0.007    | -0.123            | 0.007    |
|               | WE-150C | 0.114            | 0.005    | -0.118            | 0.006    |
|               | Ni99.2  | 0.111            | 0.006    | -0.119            | 0.009    |
| <b>ECSA 2</b> | W-50C   | 0.150            | 0.004    | -0.157            | 0.002    |
|               | W-150C  | 0.164            | --       | -0.170            | --       |
|               | WE-50C  | 0.155            | 0.013    | -0.155            | 0.013    |
|               | WE-150C | 0.138            | 0.009    | -0.146            | 0.009    |
|               | Ni99.2  | 0.146            | 0.003    | -0.159            | 0.009    |

## S7. Post-mortem analysis

Following the assessment of electrochemical stability, we conducted a thorough analysis of the anodes using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) mapping. Our observations, illustrated in Figure S6, indicate that there were no significant morphological or compositional changes in the anodes. The SEM images reveal a similar surface morphology, and the EDX mapping confirms a consistent elemental distribution across the anodes. These findings suggest that the anode maintains its structural integrity and elemental composition even after prolonged electrochemical measurements.



**Figure S6.** Morphological analysis: (a) pre-electrochemical measurements, (b) post-electrochemical measurements, (c) elemental analysis measurements.

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