

Supporting Information

The Rotating Disc Electrode: Measurement Protocols and Reproducibility in the Evaluation of Catalysts for the Oxygen Evolution Reaction

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Experimental Section

Chemicals and experimental equipment

Absolute ethanol, Nafion[®] perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water), nickel-cobalt-oxide nanopowder (<150 nm particle size, 99% trace metals basis) and potassium hydroxide (concentrate for 1 M solution) were purchased from Sigma Aldrich (Munich, Germany). Only Millipore grade water was used for preparation of electrolyte and rinsing of equipment and setups.

Working electrodes were custom-made from glassy carbon cylinders (4 mm diameter, Sigradur G from HTW, Thierhaupten, Germany) that were pressed into a PEEK sheath (10 mm diameter, Carl Spaeter, Duisburg, Germany) and contacted via stainless steel threads. Before use, electrodes were polished down to 50 nm roughness with alumina oxide polishing pastes of decreasing particle sizes (3 μm , 1 μm , and 0.05 μm from Buehler, Esslingen am Neckar, Germany) and ultrasonicated in both water and absolute ethanol for 5 minutes each. Mercury/mercury oxide reference electrodes and platinum-wire counter electrodes were purchased from CH Instruments (Austin, USA). Reference electrodes were used with 1 M KOH as inner electrolyte. Electrochemical cells were made from PEEK (Carl Spaeter, Duisburg, Germany) to avoid the presence of any glass components, which are prone to corrosion in highly alkaline environments. All cells were jacketed to allow for temperature control. Autolab potentiostats PGSTAT204 with NOVA software packages equipped with rotating electrodes were used in all electrochemical experiments (Metrohm, Filderstadt, Germany).

Electrode preparation

Electrodes were prepared by drop casting. An ink containing 5 mg/mL of nickel-cobalt-oxide was prepared consisting of 49% millipore water, 49% ethanol and 2% Nafion solution. Before use, the ink was ultrasonicated for 15 minutes and immediately used for drop casting.

Volumes of 2.5 μL were pipetted onto the cleaned electrode surface to achieve a loading of 100 $\mu\text{g}/\text{cm}^2$. The electrodes were allowed to dry at room temperature for two hours prior to experiments. Only electrodes were measured with an optically smooth film that would cover the complete glassy carbon electrode support.

The accuracy of manually prepared electrode layers by a drop-coating method, however, is limited and slight deviations in the catalyst layer formation are inevitable. A systematic documentation of the electrode appearance by photo- or micrographs was not part of the here applied protocol, but can be strongly recommended as an additional tool when analyzing error sources for possible deviations in recorded datasets.

As an example, Figure S3 shows a series of Ni-Co-O electrodes prepared by a single experimenter. It clearly can be seen that the appearance of the electrodes varies to some extent. It has to be noted here, that the presented electrodes only serve as an illustration for layer inhomogeneity, as the electrode-images were taken from a subsequent study, using PTFE as a binder instead of Nafion and rotating the electrode during the drop-coating and drying process to reduce the coffee-ring effect. Further, the electrodes shown in Figure S3 were prepared by using inks with two different binder-to-catalyst-mass ratios (0.05 for the top six electrodes and 0.2 for the bottom three electrodes), indicating differences in the quality of film formation depending on the ink composition. Optimization of film formation by testing different ink compositions can therefore be considered a prerequisite for the electrochemical characterization of new powder catalysts by RDE that should not be easily neglected.

Electrochemical characterization

Electrochemical measurements were performed according to the procedure describe in the main text. The open circuit potential (OCP) of the activated electrode is measured for 60 s along with electrochemical impedance spectroscopy (EIS) to determine the Ohmic drop. EIS is measured at the OCP, applied frequencies were from 100 kHz to 10 Hz with an amplitude of 10 mV_{RMS}. The correction of the iR drop is carried out manually after the measurement by subtracting the product of measured Ohmic drop (typicall, 7-9 Ω) and measured current from the respective measured potentials. Before CV measurements, the potential was swept from OCP to the CV starting potential with a scan rate of 5 mV/s to avoid large potential steps which could be harmful to the catalyst. Conversion of the measured potentials to the RHE scale (at pH 14) was done by adding 934 mV to the potential as measured against Hg|HgO|1 M KOH. This conversion is in accordance with literature values for the standard potential of the mercury/mercury oxide electrode in 1 M KOH, which is 107.7 mV + 0.059 V*pH^[1–3]. Individual reference electrodes were regularly crosschecked vs. a master RE, showing deviations below ± 5 mV.

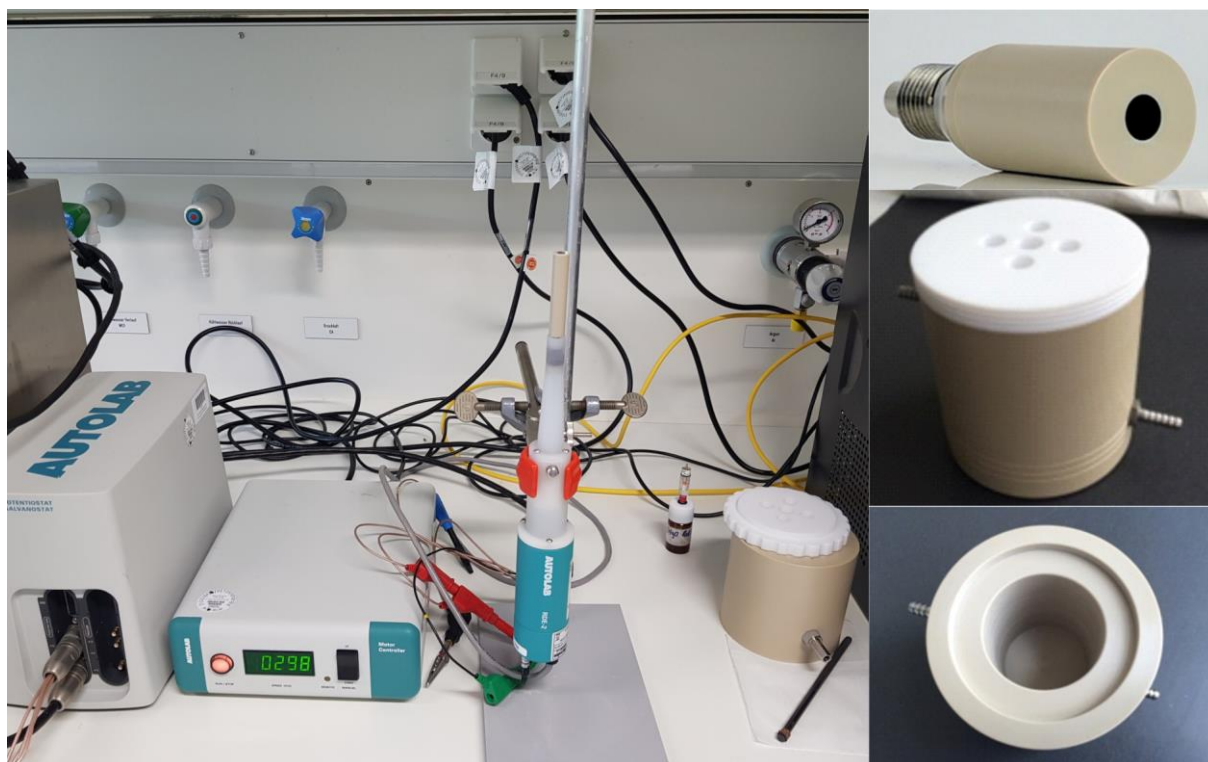


Figure S1: Photograph of the standardized setup (left) comprising an Autolab potentiostat PGSTAT204 equipped with a rotating disc electrode. As electrodes, custom-made tips of 4 mm diameter glassy carbon in a 10 mm diameter PEEK shaft were used (right, top). Experiments were carried out in a custom-made PEEK cell, which are jacketed for temperature control and equipped with a lid to allow for reproducible electrode placement (left, middle and bottom).

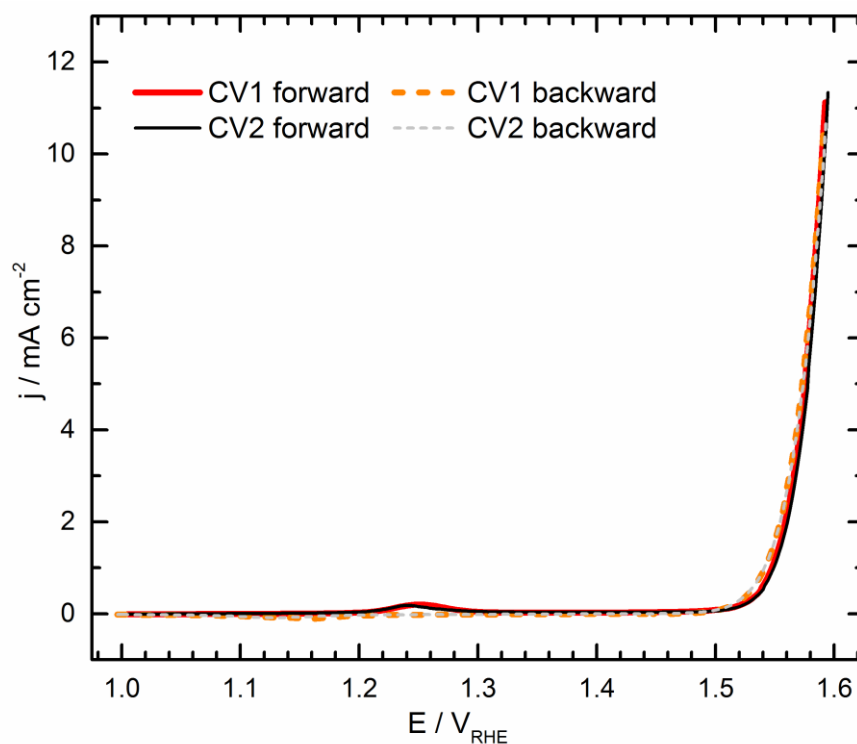


Figure S2: Forward scans (solid lines) and backward scans (dashed lines) of the cyclic voltammograms taken in the initial activity measurement step (CV1) and in the final activity measurement step (CV2).

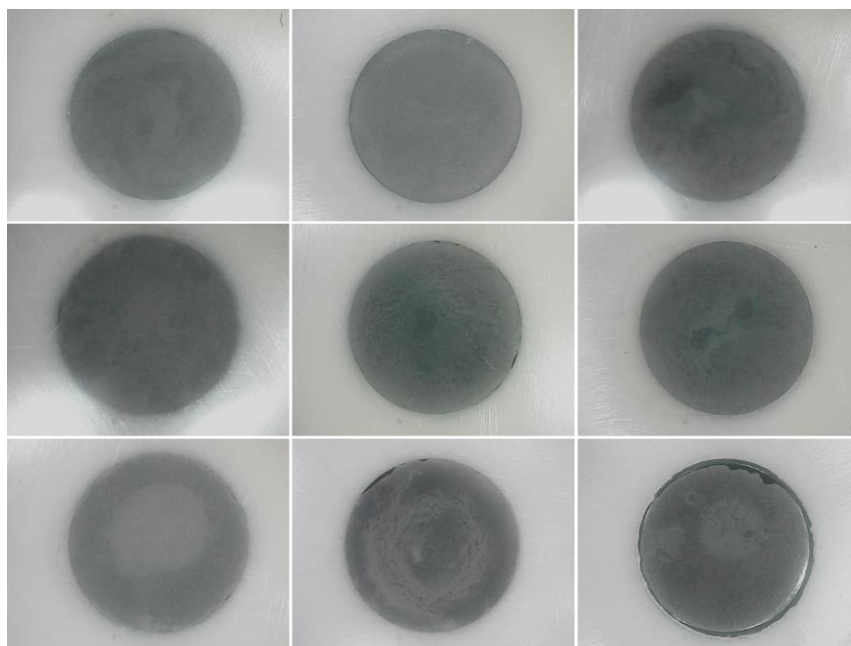


Figure S3: Photographs of different electrodes illustrating deviations in film formation. The electrodes were prepared by a single experimenter from an ink consisting of Ni-Co-O and PTFE as a binder (the binder-to-catalyst mass ratio was 0.05 for the top six electrodes and 0.2 for the bottom three electrodes). Further, the electrodes were rotated during the drop-coating and drying process.

References

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