Nickel-containing N-doped carbon as effective electrocatalysts for the reduction of CO₂ to CO in a continuous-flow electrolyzer

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Physicochemical characterization techniques

1 Thermal analysis

The as-prepared electrocatalysts were analyzed for their nickel content using a Q500 thermogravimetric analyzer (TA instruments). The temperature of the furnace was ramped from 40°C to 800°C at 5°C.min⁻¹ under a flow of air (25 sccm), after which it was kept constant until the mass change was below 0.05% min⁻¹. All samples were loaded on platinum pans. The Ni content was calculated from the residue at 800°C (after subtracting for the blank), assuming complete oxidation of Ni to NiO.

2 XRD

X-ray diffraction experiments were performed on a Huber X-ray diffractometer equipped with a G670 Guinier camera (Huber GmbH&Co, Germany) using the cu K α 1 radiation ($\lambda = 1.5405981$ Å). Each experiment had a duration of 15 min during which the image plate was scanned 3 times. In total, 4 consecutive measurements were performed and the final intensity value was the sum of all measurements. A few mg of electrocatalyst powder was dispersed in ethanol and grinded before deposition onto a 6 μ m Mylar® thin-film. Afterwards, the sample was mounted onto the sample holder and measured.

3 N₂ physisorption

Porosity and surface area measurements were performed on a Quantachrome Quadrasorb SI (Quantachrome instruments, Odelzhauze, Germany) automated gas adsorption system using liquid nitrogen as the adsorbate. All the samples were degassed in an AS-6 degasser under vacuum for 16 h at 200°C before analysis. The surface area was calculated using the BET method and the average pore size was deduced as the maximum of the BJH plots.

4 XPS

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electronics PHI 1600 multi-technique system using an Al K α (1486.6 eV) monochromatic X-ray source, operated at 15 kV and 150 W at a base pressure of 2*10⁻⁹ Torr. To correct possible deviations caused by electric charging, the graphitic C1s band at 284.6 eV was taken as internal standard. For the deconvolution and integration of the XPS signals the MultiPak software was utilized. A lot of time and effort went in to selecting those parameters (FWHM, peak position, etc.) to set to get the most accurate and reproducible results. These parameters were kept constant for the different materials. The red dash line that is visible in the deconvoluted XPS spectra is representative for the remaining difference between the fit and the actual XPS data.

5 Raman

Room-temperature Raman spectra were recorded on a LabRAM HR Evolution spectrometer from HORIBA Scientific. The spectroscope was equipped with a high stability confocal microscope with XYZ motorized stage and objectives of 10 X 50x, 100x magnification, a multichannel air cooled detector (with $< 1 \text{ cm}^{-1}$ spectral resolution) and a solid state laser with a wavelength of 532 nm (Nd:YAG). Peak integration and deconvolution was done by using the IgorPro software.

6 HAADF-STEM

The samples were dispersed in methanol and drop-casted onto transmission electron microscopy (TEM) grids. An FEI Osiris electron microscope in the scanning TEM (STEM) mode was employed to image the Ni-N-AC-C sample using a high-angle annular dark-field (HAADF) detector at 200 kV. A FEI titan electron microscope with a CEOS probe corrector was employed to acquire atomic resolution images on the Ni-N-AC-B1 in STEM mode at 300 kV. A converge angle of 22.5 mrad and a camera length of 73 mm was used for imaging. A HAADF detector with collection angle range 79-200 mrad and a low-angle ADF detector (LAADF) with collection angle range 19-74 mrad were both used for imaging. Electron energy loss spectroscopy (EELS) was used to identify the single atoms on the carbon support. The settings for EELS are 0.5 eV/channel for dispersion, 29.5 mm for the camera length, 5 mm for the EELS aperture and 100 seconds for the total acquisition time. determine the elemental distributions.



Figure S1. N₂ physisorption isotherm of N-AC-pure-B and Ni-AC-B1 (top) and BJH plots of N-AC-pure-B and Ni-AC-B1 (bottom).



Figure S2. XRD diffractogram of the different electrocatalysts. The peaks are identified as follows: Δ is metallic nickel and * is nickel hydroxide.



Figure S3. Deconvoluted XPS spectra of Ni-N-AC-B2: N1s (A) and Ni2p (B).



Figure S4. Deconvoluted XPS spectra of Ni-N-AC-B3: N1s (A) and Ni2p (B).



Figure S5. Deconvoluted XPS spectra of Ni-N-AC-C: N1s (A) and Ni2p (B).



Figure S6. Deconvoluted N1s XPS spectra of N-AC-pure-1 (A) and N-AC-pure-2 (B).



Figure S7. Full spectrum of Ni2p for Ni-N-AC-B1



Figure S8. Charging current densities plotted versus scan rate. Slopes are equal to the capacitance of the sample.

 Table S1. Capacitance values as determined by CV measurements at different scan rates and corresponding roughness factor.

Sample	Capacitance (mF/cm ²)	Roughness factor
N-AC-pure-A	42.2	2.11
N-AC-pure-B	49.4	2.45
Ni-N-AC-A	21.7	1.09
Ni-N-AC-B1	21.7	1.07
Ni-N-AC-B2	21.9	1.08
Ni-N-AC-B3	20.2	1.00
Ni-N-AC-C	32.8	1.62



Figure S9. Linear sweep voltammetry plots of Ni-N-AC-B1 in the absence and presence of CO_2 in the 0.5M KHCO₃ electrolyte.



Figure S10. Plots of normalized current density vs. potential measured in CO₂ saturated 0.1M KHCO₃.



Figure S11. Faradaic efficiencies to H₂.



Figure S12. GC chromatograms for Ni-N-AC-B1 at different potentials in the H-cell.



Figure S13. Calibration curves for CO (left) and H₂ (right) used to convert the detected peak areas of CO and H₂ into concentrations.

The calibration curves in figure S13 were determined in the same setup that was used for the measurement (however in absence of an applied potential and a catalyst) utilizing standardized gas mixtures. The GC area is plotted with respect to the available gas concentrations in the certified gas mixtures.

Sample	Tafel slope (mV dec ⁻¹)
N-AC-pure-A	360
N-AC-pure-B	267
Ni-N-AC-A	200
Ni-N-AC-B1	185
Ni-N-AC-B2	218
Ni-N-AC-B3	185
Ni-N-AC-C	287

Table S2. Tafel slope as determined from the j_{CO} - η curves.



Figure S14. (A) Normalized partial current densities to CO and (B) Faradaic efficiencies to CO measured after 25 min of chrono-amperometry experiments performed at set potentials using different electrolyte concentrations (0.1 vs. 0.5 M) and different catalyst loadings (785 µg.cm⁻² vs. 200 µg.cm⁻²).



Figure S15. Comparison between potential decay at -50 mA.cm⁻² for two different anodes in the flow-cell setup (Fumatech[®] membrane, anolyte: 2M KOH, katholyte: 1M KHCO₃).