Supporting information

Precursor-based synthesis and electrochemical nitrogen reduction reaction (eNRR) activity of compositionally complex early transition metal carbides and (carbo)nitrides

Dharma Teja Teppala,[a] Naina Goyal,[b] Minoo Boroojerdi,[a] Daniela Camacho,[a] Sanjay Mathur,[b] Emanuel Ionescu[a,c]

[a] *TU Darmstadt, Institute for Materials Science, Otto-Berndt-Str. 3, D-64287 Darmstadt, Germany*

[b] *University of Cologne, Institute for Inorganic and Materials Chemistry, Greinstr. 6, D-50939 Cologne, Germany*

[c] *TU Wien, Institute for Chemical Technologies and Analytics, Getreidemarkt 9, 164 CT, 1060 Wien, Austria*

XRD of VC and NbC

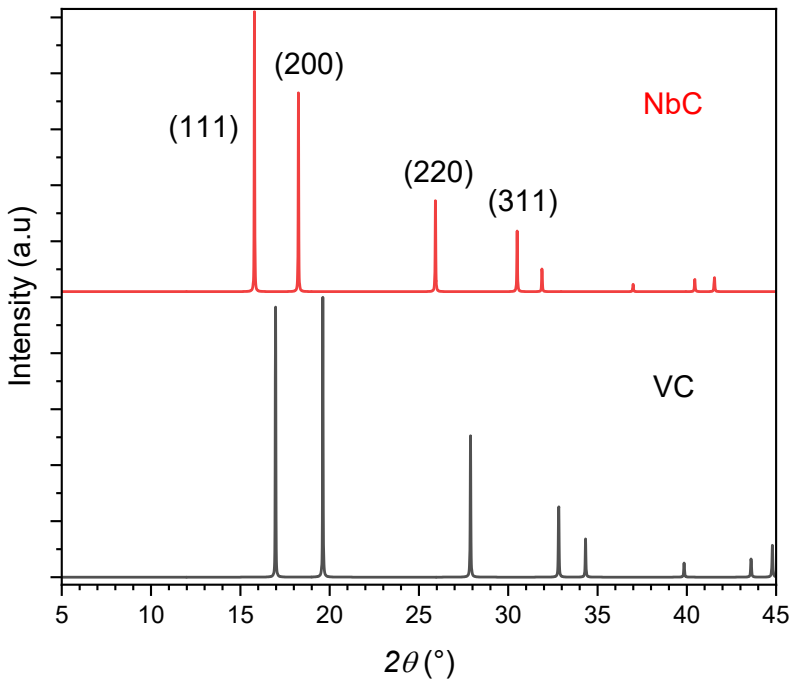


Figure S1. XRD of VC and NbC obtained from the ICSD database.

In the case of VC, I_{111}/I_{200} is lower than 1, and in the case of NbC, it is greater than 1. Strictly based on the atomic scattering factor, the I_{111}/I_{200} is always lower than 1. Still, due to the Lorentz-Polarization factor and the multiplicity factor, the introduction of Niobium increases the intensity of (111) considerably over (200). However, in the case of the I_{220}/I_{311}, the ratio is always greater than 1 in the case of a stoichiometric carbide.

Table S1. Expected and experimental lattice parameters of the synthesized carbides

Composition	Expected (Å)	Experimental (Å)	δ_a (%)
VNbTa	4.365	4.398	3.28
VNbW	4.291	4.336	3.06
VNbMoW	4.286	4.318	2.66
VNbTaMoW	4.321	4.359	2.86

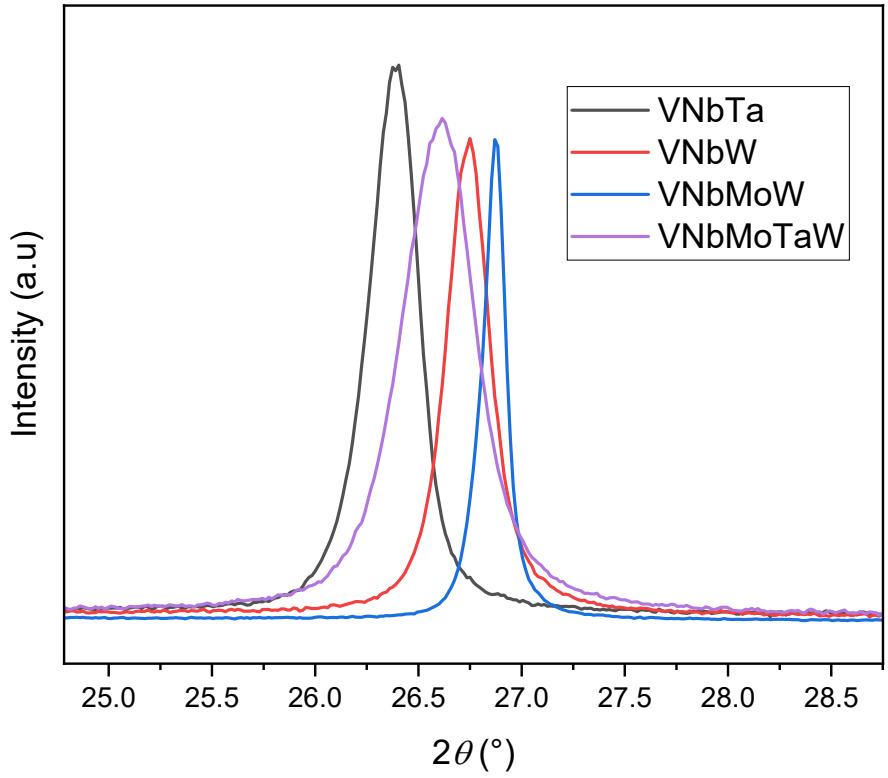


Figure S2. Shift in the Lattice parameter of samples annealed at 1700 °C with respect to elements.

Determination of ammonia:

The amount of ammonia produced was quantified using the indophenol blue method with a commercial ammonia detection kit. Typically, 5 mL of electrolyte was mixed with 0.6 mL of Reagent 1 (sodium hydroxide), followed by the addition of Reagent 2 (thymol). The mixture was left to stand for 5 min to ensure complete dissolution. Reagent 3 (2-propanol) was then added, and the solution was gently stirred. After another 5 min standing period, the absorbance was measured using UV-vis spectroscopy. The characteristic peak at ~693 nm was used to determine ammonia concentration from a calibration curve. For calibration, standard NH_4Cl solutions (0, 0.1, 0.2, 0.3, 0.4 μg mL^{-1}) were prepared in 0.1 M Na_2SO_4 and processed using the same colorimetric protocol. The resulting calibration curve was applied to calculate ammonia yield and faradaic efficiencyThe ammonia yield was calculated using the following equation:

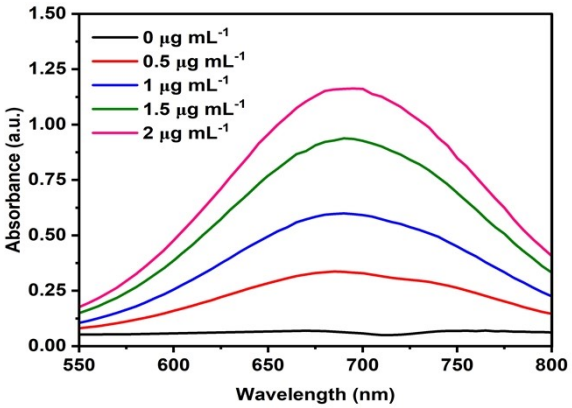
$$NH_3 yield = \frac{C_{NH_3}.V}{m_{cat}.t}$$

where C_{NH_3} is the concentration of ammonia determined from the absorbance, V is the volume of the electrolyte, m_{cat} is the mass of catalyst loaded on the electrode, and t is the duration of the chronoamperometric test.

Faradaic efficiency (FE) was calculated as the fraction of total charge used for ammonia synthesis, using the equation:

$$FE = \frac{3F.C_{NH_3}.V}{17.Q}$$

where F is the Faraday constant (96,500 C mol^{-1}), and Q is the total charge passed during the electrolysis, obtained by integrating the chronoamperometric current over time.



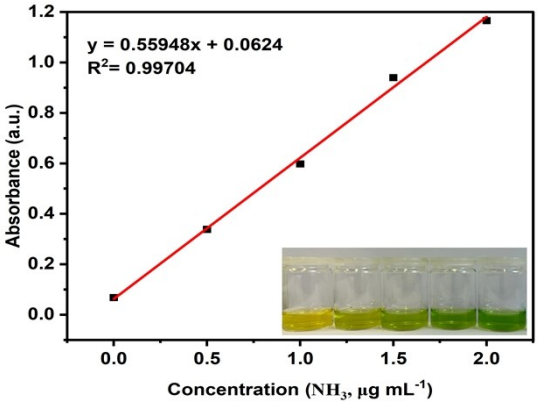


Figure S3. Ammonia production was quantified using the indophenol blue spectrophotometric method, with calibration curves employed for yield determination.

We have calculated electrochemical surface area of our best electrocatalytic performant sample. To evaluate the ECSA, the double layer capacitance (C_{dl}) was first determined by performing cyclic voltammetry (CV) in non-faradaic region (-0.5 to -0.6 V vs. Ag/AgCl) using equation $\Delta j = (j_a - j_c)/2$, where j_a and j_c are anodic and cathodic current densities at increasing scan rate from 20 to 100 mV s^{-1}. The ECSA was estimated by C_{dl}/C_s, where C_s is the specific capacitance of the flat electrode area as 0.41 mF cm^{-2} in 0.1 M Na_2SO_4. The following details are now added in supporting information including measurement data given below. The C_{dl} of 6.67 mF cm^{-2} yields in ECSA of 16.3 cm^2.

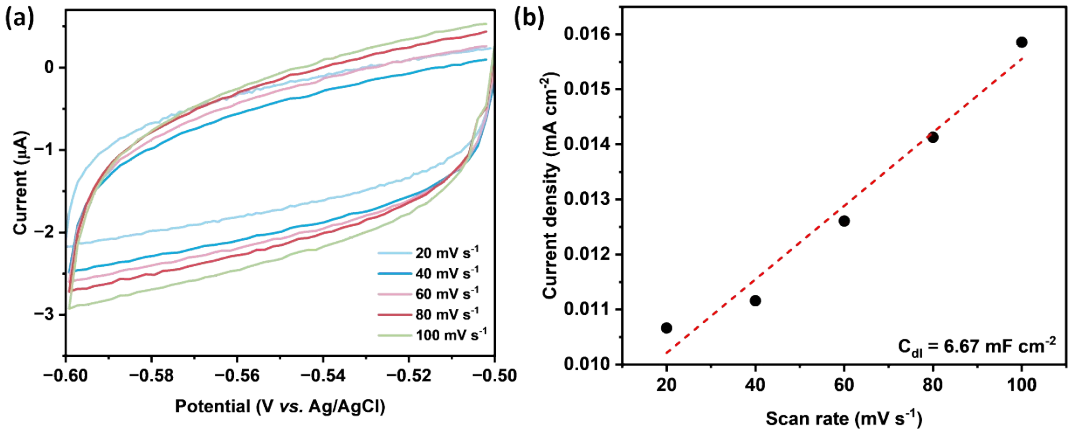


Figure S4. *(a) Cyclic voltammogram performed at different scan rate within potential window of -0.5 to -0.6 V and (b) corresponding current density vs. scan rate linear fit plot to extract C_{dl} of the electrocatalyst in 0.1 M Na_2SO_4 electrolyte.*

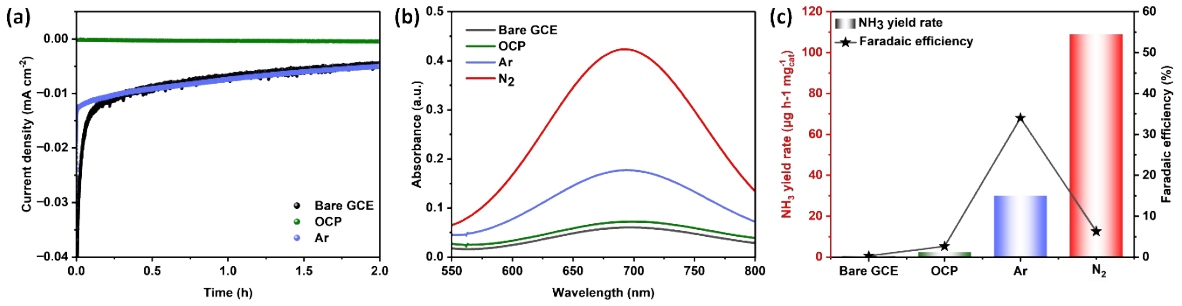


Figure S5*. (a) Chronoamperometry formed in all three conditions; open-circuit potential (OCP), Bare GCE and Ar-saturation at -0.3 V, (b) corresponding UV-Vis spectra performed for indophenol blue test and (c) NH_3 yield rate and faradaic efficiency compared with best electrocatalytic performant in N_2.*