

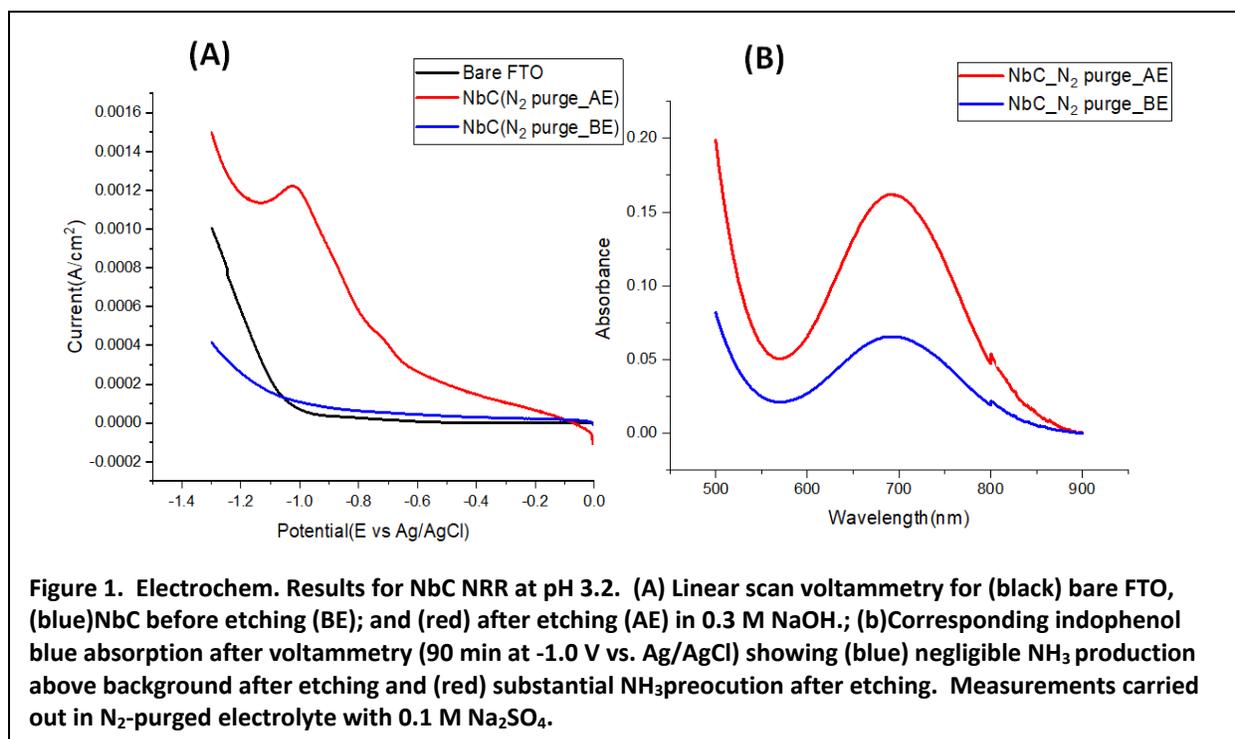
Supplemental Document: Factors Governing Transition Metal Carbide Reactivity at the Vapor/Solid and Liquid/Solid Interfaces—results of *in situ* XPS studies at the liquid/solid interface

Samar Alhowity, Ashwin Ganesan, Mojgan Gharaee, Olatomide Omolere, Qasim Adesope, Kabirat Balogun, Precious Chukwunenye, Francis D'Souza, Thomas R. Cundari, and Jeffry Kelber.

Introduction The electrocatalytic reduction of N_2 to NH_3 is an environmentally/energy-friendly alternative to the high temperature Haber-Bosch process for ammonia production, as the latter accounts for ~ 2% of world energy usage. Transition metal carbides are of broad interest for a number of catalytic and electrocatalytic applications [1,2]. We show here that ambient-exposed NbC (with a Nb_2O_5 surface layer) is NRR-inactive. However, etching in 0.3 M NaOH¹ leaves a surface Nb sub-oxide phase, which displays significant NRR activity. These experiments, which combine *ex situ* electrochemical measurements with *in situ* sample transfer between UHV and electrochemistry environments—“UHV-EC[3]”—demonstrate, in line with our previous results [4]—that *effective transition metal-based NRR catalyst surfaces exhibit metal cations in intermediate oxidation states*.

Methods NbC films were deposited in a turbomolecular-pumped magnetron sputter deposition system (base pressure ~ 2×10^{-9} Torr) equipped with a commercial DC magnetron source attached to a UHV XPS analysis chamber with AlK α source and hemispherical analyzer, permitting sample transport between sputtering and surface analysis chambers without sample exposure to atmosphere. NbC sputter deposition was done using a 99.5% purity NbC target (1.3 inches diameter, from Process Materials Inc) at a substrate temperature of ~800 K in 8 mTorr Ar gas and 30 W power for 30 minutes. Film thickness was estimated at ~ 300 Å on the basis of estimated sputtering rates, XPS, and XRD data. *Ex situ* electrochemical studies were carried out at pH 3.2 (0.1 M Na_2SO_4) using procedures described previously [4]. Ammonia production was measured by UV-VIS absorption using the indophenol blue dye method [4]. Extensive precautions were taken to avoid false positive due to incidental NH_3 , NO_3^- or NO_2^- contamination [4]. UHV-EC measurements were carried out with similar NbC films using a separate electrochemical/UHV-XPS system described previously [3].

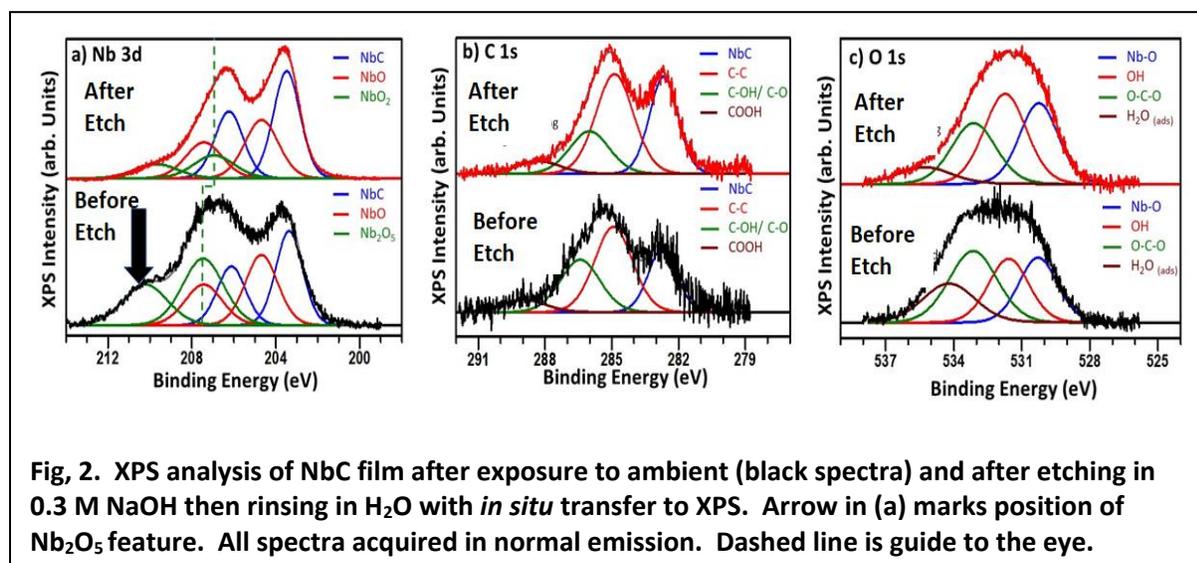
Results: XPS, XRD and SEM data (not shown here) indicate that NbC films as deposited, showed the



Nb-oxide related XRD peaks indicative of Nb oxide phases interspersed throughout the film. (TaC films

did not exhibit such oxide-related XRD features, consistent with enhanced NbC reactivity towards oxygen relative to TaC.) NbC electrochemical data are shown in Fig. 1. The linear scan voltammetry (Fig. 1A) demonstrates that the ambient-exposed NbC sample, unetched (blue trace), displays no significant electrochemical activity at cathodic potentials < -1.0 V vs Ag/AgCl. In contrast, the sample etched in 0.3 M NaOH immediately prior to testing (red trace) exhibits significant NRR activity in this potential range. Corresponding measurements of NH_3 production at -1.0 V vs. Ag/AgCl (Fig. 1b) demonstrate that the unetched sample (blue trace) displays no significant NH_3 production (above background) while the etched sample (red trace) displays significant NH_3 production (Faradaic Efficiency $\sim 3.2\%$). Thus, the data in Fig. 1 demonstrate that a NbC surface exposed to ambient is NRR inactive, but that etching in 0.3 M NaOH, results in electrocatalytic activity.

Corresponding UHV-EC XPS results are displayed in Fig. 2. The data show that the NbC exposed to ambient exhibits (black traces) both adventitious C and a Nb_2O_5 surface layer (Fig. 2a, arrow). This Nb_2O_5 layer, present after ambient exposure on the unetched sample is correlated with inhibited NRR activity (Fig. 1). In contrast, after ~ 1 min immersion in 0.3 M NaOH at open circuit potential, followed by emersion, rinsing in DI water and *in situ* transport to the XPS chamber (Fig. 2) the etched



surface (red traces) exhibits only intermediate Nb oxidation states, leading to enhanced NRR activity (Fig. 1). Significant adventitious C remains, but this does not destroy NRR activity.

Conclusion: The data shown in Figs. 1 and 2 demonstrate that Nb metal cations stabilized in *intermediate oxidation states* are NRR active. Further studies of metal carbide and related surfaces as NRR catalysts are in progress in our laboratories.

References

1. C. Kunkel, et al., *Energy Environ. Sci.* 2016, 9, 141–144.
2. J. A. Rodriguez, et al., *ACS Catal.* 2015, 5, 6696–6706
3. J. Kelber and G. Seshadri, *Surf. and Interf. Anal.* **31** (2001) 431-441
4. P. Chukwunye, et al., *J. Mater. Chem. A.* **10** (2022) 21401-21415

Acknowledgement This work was supported in part by the UNT College of Science through COS grants 1600089 and RSG-2023-002 and in part by the NSF under grant no. DMR 2112864.