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## **NAP-XPS study of the interaction of molecular nitrogen with vanadium oxide in the absence and presence of water vapor at room temperature**

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Interactions of N<sub>2</sub> and H<sub>2</sub>O at transition metal oxide surfaces are of fundamental interest for gaining insight into electrocatalytic nitrogen reduction reaction (NRR) mechanisms. N<sub>2</sub>/H<sub>2</sub>O interactions at the polycrystalline vanadium oxide/vapor interface were monitored at room temperature and N<sub>2</sub> partial pressures between 10<sup>-9</sup> Torr and 10<sup>-1</sup> Torr using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The oxide film was predominantly V(IV), with significant V(III) and V(V) components. Such films have been previously demonstrated to be NRR active at pH 7. There is little understanding, however, of the detailed nature of N<sub>2</sub>-surface interactions. XPS measurements were acquired at room temperature in environments of both pure N<sub>2</sub> and equal pressures of N<sub>2</sub> and H<sub>2</sub>O vapor, up to a N<sub>2</sub> partial pressure of 10<sup>-1</sup> Torr. In the absence of H<sub>2</sub>O, broad N 1s features were observed at binding energies of 401 eV and 398.7 eV with relative intensity ratios of ~ 3:1, respectively. These features remained upon subsequent pumpdown to 10<sup>-9</sup> Torr, indicating that adsorbed nitrogen is stable at room temperature in the absence of equilibrium with gas phase N<sub>2</sub>. In the presence of equal pressures of N<sub>2</sub> and H<sub>2</sub>O vapor, the 401 eV N 1s feature was reduced in intensity by ~ 50% at 10<sup>-1</sup> Torr N<sub>2</sub> partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N<sub>2</sub>-surface binding in the absence of N<sub>2</sub> overpressure are consistent with N<sub>2</sub> binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N<sub>2</sub>/H<sub>2</sub>O binding is competitive. SCF-HF calculations suggest that the two N 1s XPS features correspond to “shake” and normal transitions at 401 eV and 398.7 eV, respectively, for N<sub>2</sub> bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N<sub>2</sub> pi\* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N<sub>2</sub> -V(III) binding. The data presented demonstrate the ability of NAP-XPS, in concert with theory, to provide atomic-level insight concerning interfacial reactions relevant to electrocatalysis.

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**if “Other”, please specify:**

**I apply for a travel grant**

No

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