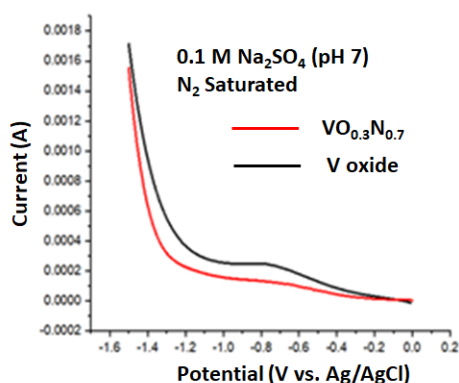


## Mechanisms of Electrocatalytic Reduction of N<sub>2</sub> at Vanadium and Cobalt Oxynitride Surfaces: Impacts of Metal Oxophilicity and $\pi$ -Backbonding

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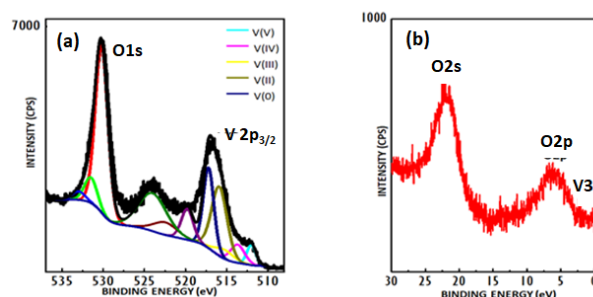
The electrochemical reduction of N<sub>2</sub> to NH<sub>3</sub>—the nitrogen reduction reaction (NRR)—is of burgeoning interest as an environmentally/energy-friendly alternative to the Haber-Bosch process, which currently accounts for ~2% of the world's energy consumption, with heavy consumption of fossil fuels due to running at elevated temperatures [1]. Earth-abundant oxides and oxynitrides have been the objects of intensive study over the last 3 years, but major uncertainties remain, including (a) the roles of



**Fig. 2. Electrochemical polarization curves for N-free vanadium oxide (black trace) and for a VO<sub>0.3</sub>N<sub>0.7</sub> film. From [6].**

but also selectivity against the Hydrogen Evolution Reaction (HER).

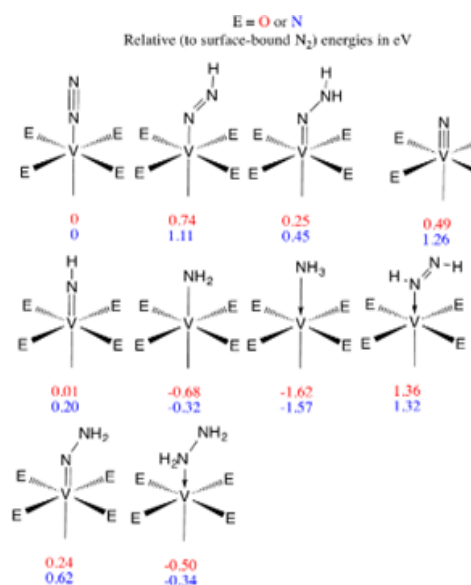
To begin to explore this area in a systematic manner, we have prepared vanadium oxynitride (VO<sub>x</sub>N<sub>1-x</sub>) and CoO<sub>x</sub>N<sub>1-x</sub> films (0 < x < 1), characterized by AES, XRD, and XPS, using magnetron sputter deposition [2, 3]. Variations in O<sub>2</sub>/N<sub>2</sub> plasma pressures have been used to systematically vary x [2, 3]. Electrochemical polarization measurements have been carried out in pH 7 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolytes to minimize HER effects. In general, the vanadium oxide and oxynitride films exhibit similar V 2p and O1s core level spectra (e.g., Fig. 1 for x = 1)[3, 4] with V in both +3 and +4 oxidation states. Oxynitride films (x < 1) exhibit N 1s peak binding energies near 397.0 eV [3] in close agreement with previous studies of VN films (not shown) [5]. Electrochemical polarization curves (Fig. 2) are similar for both species, though slightly higher for the N-rich film. (The direct production of NH<sub>3</sub> was confirmed by absorption spectroscopy,) This is consistent with our findings that both lattice N and



**Fig. 1 XPS spectra of a Vanadium oxide film prior to immersion in electrolyte: (a) O 1s/V 2p ; (b) valence band. Both V(III) and V(IV) are present. From [4]**

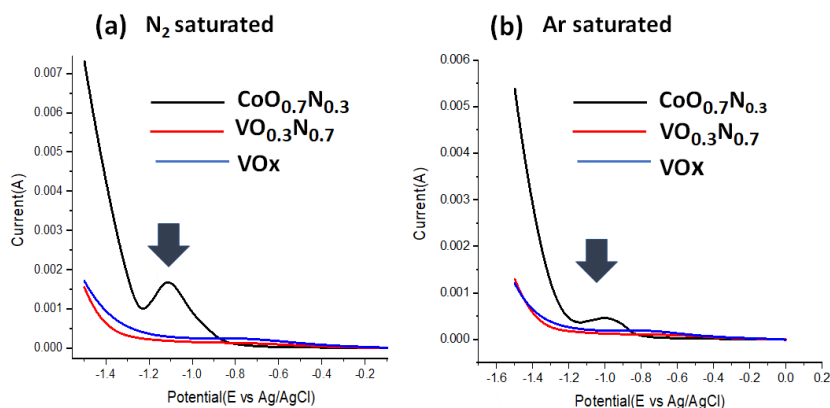
O-metal and N-metal interactions in the NRR process, and (b) the effects of  $\pi$ -backbonding in metal-N<sub>2</sub> adsorption and reactions.

Such factors may impact not only NRR activity,



**Fig. 3 Configurations of various possible N/H intermediates in NRR. Calculated relative energies (in eV) are also shown relative to that of surface bound N<sub>2</sub> are shown for both E = O (red), [V]<sub>o</sub>, and E =**

solvated  $N_2$  undergo reduction predominantly at O-supported vanadium centers ( $V_O$ ) rather than at N-supported vanadium centers ( $V_N$ ) [6]. DFT-based calculations [4] indicate that  $N_2$  adsorption and protonation are energetically favored at  $V_O$  vs.  $V_N$  centers (Fig. 3) consistent with the somewhat enhanced activity for the vanadium oxide film vs. the oxynitride film (Fig. 3).



**Fig. 4** EC polarization curves for  $CoO_xN_y$  (black trace),  $VO_{0.3}N_{0.7}$  (red) and V oxide (blue). Same conditions as in Fig. 3. Region near -1.1 V (arrow) shows greater intensity in  $N_2$ -saturated vs.  $H_2$ -saturated solution, indicating NRR selectivity.  $NH_3$  detected by absorption spectroscopy (not shown). (Unpublished)

however, exhibit greater 3d-orbital occupancy for cations of comparable charge (e.g., Co(III) vs. V(III)), suggesting greater  $\pi$ -backbonding, which should enhance  $N_2$ -M attraction and weaken NN bonds, thus enhancing initial N protonation. Electrochemical polarization curves (Fig. 4) show an ***order of magnitude increase in NRR activity*** in  $N_2$ -saturated pH 7 electrolyte for  $Co_{0.7}N_{0.3}$ . Further, regions near -1.1 V vs Ag/AgCl (arrow, Fig. 4) show greater intensity in  $N_2$ -vs.  $H_2$ -saturated solution, indicating significant selectivity for NRR. The data demonstrate greatly enhanced NRR activity and selectivity for the  $CoO_xN_y$  film, strongly suggesting the importance of M- $N_2$   $\pi$ -backbonding in NRR. This relationship is being explored in experiments underway in our laboratories.

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The data in Figs. 1-3 demonstrate that for oxophilic metals,  $V_O$  sites are preferred vs.  $V_N$  sites for  $N_2$  adsorption and reaction, although this preference may become less pronounced for less oxophilic metals toward the right of the periodic table. Metals toward the right of the periodic table,