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## Journal of Materials Chemistry A

# ARTICLE



# Vacancy Diffusion Barriers in TaON and Ta<sub>3</sub>N<sub>5</sub> Water-Splitting **Photocatalysts**

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Mixed anion semiconductors such as oxynitrides offer a wide range of properties that can be tuned for various catalytic applications, such as photocatalytic water splitting. In this work first-principles simulations are used to predict the competing stabilities and mobilities of nitrogen and oxygen anion vacancies in the archetypal (oxy)nitride photocatalysts TaON and  $Ta_3N_5$ . The results demonstrate how the local  $Ta^{5+}$  coordination environment, vacancy defect charge and the anion coordination number each influence the dominant ionic diffusion mechanism in both TaON and Ta<sub>3</sub>N<sub>5</sub>. Defect charge is intrinsically tied to the nature and kinetics of defect migration in these materials. Specifically, for neutral and low-charge defects in TaON, oxygen anion diffusion dominates ionic mobility, while higher charge states impede oxygen diffusion and simultaneously lower nitrogen diffusion barriers. This result provides a potential explanation for why TaON and Ta<sub>3</sub>N<sub>5</sub> (and related (oxy)nitrides) are prone to becoming nitrogen deficient under catalytic operating conditions. Charge additionally stabilises oxygen anti-site defects in TaON, and oxygen impurity defects in Ta<sub>3</sub>N<sub>5</sub>, which is consistent with the tendancy of these materials to undergo oxidative decomposition, reforming pure oxide compounds such as Ta2O5. These insights highlight the importance of metal ion coordination and structural packing in retaining nitrogen content in oxynitride semiconductors for enhanced stability.

## Introduction

Oxynitride materials have attracted recent interest for use in applications such as pigments, dielectrics, and optoelectronic materials.1 The overlap between the band gaps of many oxynitride materials and the solar spectrum also makes them potential water splitting photocatalysts that can operate in the visible-light region.<sup>2</sup> Notably, TaON and Ta<sub>3</sub>N<sub>5</sub> respectively possess band gaps of 2.1 and 2.4 eV and absorption edges of 510 and 600 nm, respectively.<sup>1</sup> This affords high photocatalytic activities for water oxidation using both materials, with TaON and Ta<sub>3</sub>N<sub>5</sub> exhibiting quantum efficiencies of 34 and 10% under visible-light irradiation.<sup>3</sup> More generally, band gaps for tantalum (oxy)nitrides range from 2.5 to 1.9 eV, corresponding to theoretical solar-to-hydrogen efficiencies of 9.3 to 20.9%.<sup>4</sup>

TaON and Ta<sub>3</sub>N<sub>5</sub> can be prepared by nitridation of Ta<sub>2</sub>O<sub>5</sub> powders under flowing  $NH_3$  at temperatures above 973 K.<sup>3</sup> Such materials are therefore prone to oxidative decomposition, via reformation of Ta<sub>2</sub>O<sub>5</sub> and evolution of N<sub>2</sub>. <sup>5</sup> The Ta<sub>2</sub>O<sub>5</sub> layers thus formed at the catalytic interface hinder hole transport to the electrolyte, reducing the overall photocatalytic performance of the material. There are a number of likely causes of such oxidative decomposition. Compared to their parent oxide compounds, the band gap of (oxy)nitrides is reduced, since the N-2p orbitals are higher in energy than the O-2p orbitals. Increasing nitrogen content therefore increases the N-2p character in the valence band and decreases the oxidative stability of the material.<sup>6</sup> Further, O<sub>N</sub> anti-site defects in TaON (in which an O<sup>2-</sup> anion resides in a N<sup>3-</sup> vacancy defect site) have low formation energies under typical photocatalytic operating conditions.<sup>7, 8</sup> The fact that TaON and Ta<sub>3</sub>N<sub>5</sub> can support high defect densities has itself driven research into development of perovskite oxynitrides  $AB(O,N)_3$  (A = Ca, Sr, Ba, and La, B = Ti, Ta, & Nb) as photocatalytic materials, due to the structural modulation afforded by the A-site cation.9

Despite their tendency for oxidative decomposition, there is evidence suggesting that oxynitride materials exhibit improved ionic conductivity. For instance, Kilo et al.<sup>10</sup> have shown that the ionic mobility of O<sup>2-</sup> anions in yttria-stabilized zirconia (YSZ) are lower than that in its oxynitride counterpart, YZrON. Importantly, this study showed that the dominant conducting ion under standard photocatalytic conditions in both YSZ and YZrON is O<sup>2-</sup>, and not N<sup>3-</sup>. Despite having a large influence on the diffusion kinetics of the O<sup>2-</sup> anions, the N<sup>3-</sup> anion plays a more structural role. Kageyama et al.<sup>11</sup> have noted a similar conclusion, viz. that in a mixed-anion material, one anion will dominate ionic mobility, while the other imparts structural stability.

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#### ARTICLE

The different roles played by anions in a mixed anion material therefore provide a convenient design parameter for developing new photocatalytic materials. However, fundamental thermokinetic aspects of mixed ion diffusion in oxynitride materials, such as vacancy defect migration barriers and formation energies, remain largely unexplored. Nevertheless, it is likely that they play an important role in determining photocatalytic activity, as is the case for oxide photocatalysts.<sup>12-17</sup>

Herein, this shortcoming is addressed by predicting the vacancy defect diffusion barriers in bulk TaON and  $Ta_3N_5$  using first principles calculations. A principle aim of this study is to understand and quantify the competition between simultaneous O<sup>2-</sup> and N<sup>3-</sup> anion vacancy diffusion barriers in TaON, and how this competition is influenced by the charge state of the material. It is found that the migration of N<sup>3-</sup> vacancy defects are extremely sensitive to the charge state, with diffusion barriers deviating by several eV. By contrast, the diffusion of oxygen vacancy defects is largely independent of the charge state. Additionally, the formation of oxygen anti-site defects is charge modulated; at high charges, such defects are thermodynamically favourable. However, this is never the case for nitrogen anti-site defects, which become increasingly unfavourable with increasing charge state. In Ta<sub>3</sub>N<sub>5</sub>, vacancy defect diffusion is shown to be kinetically anisotropic, since diffusion barriers are determined by the nominal coordination numbers in the vicinity of the defect. This is also the case for the diffusion of oxygen impurities. These results provide a basis for understanding how structural and coordination effects can tune the mobility of oxygen and nitrogen anions relative to each other in TaON, Ta<sub>3</sub>N<sub>5</sub> and tantalum perovskite oxynitrides more generally.

## Methodology

All calculations reported here employ the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) exchange correlation functional, revised for solids (i.e. PBEsol),18 as implemented in the Vienna Ab-initio Simulation Package (VASP) code<sup>19, 20</sup> using the projector augmented wave (PAW) method.<sup>21</sup> All calculations employ (core)/valence configurations of Ta: ([Ne]3s)/3p3d4s; O: ([He])/2s2p N: ([He])/2s2p and a plane wave energy cutoff of 400 eV. Crystal structures of  $\beta$ -TaON and  $\beta\text{-}Ta_3N_5$  at standard conditions were obtained from the International Crystal Structure Database (ICSD crystal IDs 192423 and 16253, respectively), see Figure 1.<sup>22</sup> Following Chen et al.<sup>23</sup> we employ a 96 atom  $2 \times 2 \times 2$  TaON supercell (P<sub>21/c</sub> space group). For  $Ta_3N_5$  we employ a 64 atom  $2 \times 2 \times 1$   $Ta_3N_5$  supercell ( $C_{mcm}$  space group). Since our focus here for  $Ta_3N_5$  is the migration of N<sup>3-</sup> vacancy defects, rather than interstitial defects, the  $2 \times 2 \times 1$  Ta<sub>3</sub>N<sub>5</sub> supercell is built from the primitive unit cell and not the non-primitive unit cell. Nevertheless, Jing et al.8 have shown that N<sup>3-</sup> anion vacancy formation energies are

largely invariant to the size of the Ta<sub>3</sub>N<sub>5</sub> supercell, so we deem the size of the Ta<sub>3</sub>N<sub>5</sub> supercell employed here to be sufficient. Monkhorst-Pack meshes consisting of 5×5×5 and 4×4×4 k-points were used for the TaON and Ta<sub>3</sub>N<sub>5</sub> supercells, respectively. Both the 2×2×2 TaON and 2×2×1 Ta<sub>3</sub>N<sub>5</sub> supercells were fully optimised using PBSsol.

To model charged states of TaON and Ta<sub>3</sub>N<sub>5</sub>, we follow the approach commonly reported in the literature. The image charge correction proposed by Makov-Payne<sup>24</sup> is used to account for charged defects in the finite-sized supercell, using PBEsol static dielectric constants  $\varepsilon_0$  (trace averaged) of 24.031 (TaON) and 45.594 (Ta<sub>3</sub>N<sub>5</sub>). These  $\varepsilon_0$  values calculated here for PBEsol are consistent with values recently reported in the literature.<sup>25</sup> While the Makov–Payne correction generally includes monopole and quadrupole corrections for cubic structures, only the monopole correction can be correctly calculated for non-cubic supercells, such as that of Ta<sub>3</sub>N<sub>5</sub>, using VASP. Thus, only monopole corrections are included the image charge correction for all results reported here, consistent with other studies.<sup>7, 26, 27</sup> However, we do not anticipate this correction to significantly influence our results for Ta<sub>3</sub>N<sub>5</sub>, since the quadrupole correction is typically only ~30% of the monopole correction.28

All vacancy defect migration barriers were calculated using the Climbing Image Nudged Elastic Band (CI-NEB) method.<sup>29</sup> Migration pathways were considered based on conceivable exchange between symmetrically-distinct vacancy positions in each structure at both oxygen sites and nitrogen sites (i.e. Vo and V<sub>N</sub>, respectively). Specifically, vacancy migration pathways that could be described as a combination of shorter pathways have not been considered in this work. A comparison of V<sub>0</sub> migration in bulk Ta<sub>2</sub>O<sub>5</sub> has been excluded in this work due to ambiguities in theoretical predictions of the band gaps and phase stabilities of  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> and  $\epsilon$ -Ta<sub>2</sub>O<sub>5</sub>.<sup>30, 31</sup> Also, it is noted that a previous DFT investigation into this material reported Vo migration barriers in thin film orthorhombic Ta<sub>2</sub>O<sub>5</sub> model to be 1.0-2.5 eV.<sup>32</sup> NEB pathways for all diffusion barriers reported here are provided in Electronic Supplementary Information (ESI).<sup>+</sup>



Figure 1. Unit cells of (a) TaON and (b)  $Ta_3N_5$ .



Charge Figure 2. (a) V<sub>0</sub> migration pathways in bulk TaON, corresponding to coordination rearrangement around Ta<sup>5+</sup> ions and between TaO layers (left) and diffusion barriers as a function of the charge state (right). (b) VN migration pathways in bulk TaON (left) and diffusion barriers as a function of the charge state (right). VN pathways are limited by the greater coordination between N<sup>5</sup> and Ta<sup>5+</sup> ions, and the structure of the TaN sublattice preventing interlayer diffusion. Vacancy charge is denoted using Kröger-Vink notation. Lines are provided to guide the eye. Complete NEB pathways are provided in Figure S1 & S2.

#### **Results and discussion**

#### $V_{\text{O}}$ and $V_{\text{N}}$ Diffusion Barriers in Bulk TaON

Figure 2(a) and (b), respectively show the energy barriers associated with  $V_0$  and  $V_N$  diffusion in bulk TaON. Figure 2(a) presents a cross-sectional view of the TaO layer in TaON; the diffusion barriers reported here correspond to diffusion within this TaO layer. Interlayer Vo migration is found to be prohibitively unfavourable without a facilitating vacancy in the bridging TaN layer. V<sub>0</sub> diffusion around a common  $Ta^{5+}$  ion is considered here (i.e. between positions  $V_{01}$ ,  $V_{02}$ ,  $V_{03}$ ), as is diffusion between neighbouring Ta5+ ions (i.e. between positions V<sub>01</sub>, V<sub>02</sub>, V<sub>05</sub>). Supplementary simulations (not shown) show that interlayer  $V_0$  diffusion, i.e. between adjacent TaO layers, in TaON is kinetically unfeasible without a complimentary N<sup>3-</sup> vacancy in the adjacent TaN layer, and so these pathways are not considered further here. Figure 2(b) details the diffusion barriers for nitrogen vacancy  $(V_N)$  diffusion in bulk TaON. There are fewer distinct pathways considered in this case, since each  $N^{3-}$  anion is coordinated to four  $Ta^{5+}$  cations (whereas O<sup>2-</sup> are only coordinated to three), and the structure of the TaN sublattice effectively prevents interlayer  $V_N$ diffusion; attempted simulations of interlayer diffusion exceeded 6 eV. This means that the only feasible  $V_{\text{N}}$  diffusion pathways in TaON correspond to coordination rearrangement around a single Ta<sup>5+</sup> site.

As anticipated, Figure 2(a) shows that  $V_0$  diffusion around a common Ta<sup>5+</sup> coordination site is far more labile compared to diffusion between adjacent Ta<sup>5+</sup> ions. These pathways constitute a Ta<sup>5+</sup> coordination rearrangement. For instance, in

the neutral charge state, diffusion paths between V<sub>01</sub>, V<sub>02</sub> and  $V_{03}$  positions have barriers between 1.34-1.75 eV. These barriers steadily decrease to only 0.89-1.36 eV in the highest charge state considered here (i.e.  $V_0^{\bullet\bullet}$ ), and so are expected to dominate the V<sub>0</sub> diffusion mechanism under such conditions. In the neutral material, barriers for coordination rearrangement are ~1-1.5 eV lower than those preventing interlayer diffusion (i.e. the cavity crossing pathways), from  $V_{\rm 01}$  to  $V_{\rm 04}$  or  $V_{\rm 05}$  (~3.2 and 3.9 eV, respectively). Further, such inter-layer pathways are less sensitive to the vacancy charge. These results indicate that Vo diffusion in bulk TaON likely proceeds predominantly via coordination rearrangement pathways, and that Vo diffusion to a cavity-crossing position occurs via hopping between adjacent coordination sites. It is also likely that O<sup>2-</sup> / V<sub>0</sub> exchange does not occur via an interstitial intermediate since the interstitial substitution would also occur via the cavity space.

The two feasible  $V_N$  diffusion pathways,  $V_{N1} \rightarrow V_{N2}$  and  $V_{N1} \rightarrow V_{N3}$ , in bulk TaON are considered in Figure 2(b). In the neutral material,  $V_N$  migration via these pathways are prevented by barriers of 2.01 and 2.64 eV, respectively. This is notably higher than the neutral state  $V_0^{\times}$  barriers shown in Figure 2(a), meaning that O<sup>2-</sup> diffusion is the likely dominant contributor to ionic mobility in TaON, consistent with previous results for YZrON.<sup>10</sup> Figure 2(b) also shows that the barriers of singly charged nitrogen vacancies,  $V_N^{\bullet}$ , are comparable to the neutral barriers. Interestingly however, the diffusion barriers for doubly and triply charged nitrogen vacancy defects, i.e.  $V_N^{\bullet\bullet}$  and  $V_N^{\bullet\bullet\bullet}$ , via these pathways are lowered consistently by ~1 and ~1.4 eV. This trend is due to the reduction of coordinating Ta<sup>5+</sup> ions around the defect.  $V_N^{\times}$  and  $V_N^{\bullet}$  defects formally reduce the coordinating 5d<sup>0</sup>6s<sup>0</sup> Ta<sup>5+</sup> ions with 3e<sup>-</sup> and 2e<sup>-</sup>, respectively. However, Bader charge analysis shows that Ta<sup>5+</sup> reduction in the TaON supercell is actually comparable in the presence of the  $\ V_N^{ imes}$  and  $V_N^{ullet}$ defects, due to the delocalised occupation of Ta<sup>5+</sup> 5d states that extends beyond the immediate vicinity of the defect site. Consequently, the barriers preventing diffusion of these defects are similar. On the other hand, Ta<sup>5+</sup> reduction in the presence of  $V_N^{\bullet\bullet}$  and  $V_N^{\bullet\bullet\bullet}$  defects is less extensive and more localised around the vacancy defect site. This makes the structural distortion necessary for vacancy diffusion easier, and yields a lower diffusion barrier. Of course, the oxidation state of Ta5+ remains unchanged in the presence of a  $V_N^{\bullet\bullet\bullet}$  defect, which leads to the lowest diffusion barrier shown in Figure 2(b).

The diffusion of  $V_N^{\bullet\bullet}$  and  $V_O^{\bullet\bullet}$  defects in TaON are kinetically competitive, both being prevented by barriers of ~1 eV (depending on the diffusion pathway). However, the diffusion of  $V_N^{\bullet\bullet\bullet}$  defects is kinetically the most favourable diffusion mechanism in TaON. Thus, while ionic mobility predominantly arises from  $O^{2-}$  diffusion in neutral TaON, our results indicate this switches to  $N^{3-}$  diffusion in regions comprising higher charge states, such as near surfaces and catalytic interfaces. It is of note that this is consistent with the experimentally observed  $N^{3-}$  depletion from active TaON and Ta<sub>3</sub>N<sub>5</sub> catalytic surfaces, and the tendency for oxidative decomposition of these materials, forming oxide species such as  $Ta_2O_5,$  under electrochemical operating conditions.  $^{33\cdot35}$ 

#### Formation of Anti-site Defects and Vacancy Exchange in Bulk TaON

The stability and mobility of vacancy exchange in bulk TaON are now considered. This process converts nitrogen vacancy defects into oxygen vacancy defects, and vice versa, via the formation of anti-site  $O_N$  and  $N_O$  defects,

$$V_N \rightarrow O_N + V_o$$
 (1)

$$V_0 \rightarrow N_0 + V_N$$
 (2)

where  $O_N$  denotes an  $O^{2-}$  anion residing in a nitrogen position (enabled by the original  $V_N$  defect), and  $N_O$  denotes an  $N^{3-}$  anion residing in an oxygen position enabled by the original  $V_O$  defect). Figures 3 and 4 report formation energies and diffusion barriers for reactions (1) and (2), respectively. These figures represent slices of the  $2 \times 2 \times 2$  TaON supercell used for clarity to show the neighbouring anions considered.



**Figure 3.** (a) Migration pathways for vacancy exchange in bulk TaON via  $O^{2-}$  diffusion into a  $V_N$  defect, forming an  $O_N / V_O$  defect. (b) Formation energy and (c) diffusion barriers (right) of this vacancy exchange as a function of the  $O^{2-}$  position and TaON charge state. Formation energies are given relative to the formation energy of the  $V_N$  defect. Vacancy charge is denoted using Kröger-Vink notation. Lines are provided to guide the eye. Complete NEB pathways are provided in Figure S3.



**Figure 4.** (a) Migration pathways for vacancy exchange in bulk TaON via N<sup>3-</sup> diffusion into a V<sub>0</sub> defect, forming a N<sub>0</sub> / V<sub>N</sub> defect pair. (b) Formation energy and (c) diffusion barriers (right) of this vacancy exchange as a function of the N<sup>3-</sup> position and TaON charge state. Formation energies are given relative to the formation energy of the V<sub>0</sub> defect. Vacancy charge is denoted using Kröger-Vink notation. Lines are provided to guide the eye. Complete NEB pathways are provided in Figure S4.

Figure 3(b) shows that formation energies O<sub>N</sub> anti-site defects depend strongly on the TaON charge state. Critically, while such vacancies are endothermic for  $V_N^{\times}$  and  $V_N^{\bullet}$  vacancies, they are expected to be spontaneous for  $V_N^{\bullet \bullet}$  and  $V_N^{\bullet \bullet \bullet}$  vacancies, with formation energies as low as ~-0.8 eV, relative to the formation energy of the vacancy defect itself. There is no significant dependence on the O<sup>2-</sup> position in this respect, although formation of the O<sub>N</sub> defect using the V<sub>01</sub> O<sup>2-</sup> anion is consistently ~0.3 eV less favourable for all charge states considered. The existence of such stable O<sub>N</sub> anti-site defects in TaON, whereby O<sup>2-</sup> anions "steal" N<sup>3-</sup> positions, is consistent with the tendency of this material to undergo oxidative decomposition, forming Ta<sub>2</sub>O<sub>5</sub>. Interestingly, the O<sub>N</sub> formation energies shown in Figure 3(b) exhibit the same dependence on the vacancy defect charge as do the V<sub>N</sub> diffusion barrier heights, shown in Figure 2(b). This suggests that the principle factor determining the stability of these defects is the location of the vacancy in the TaON lattice, rather than the defect exchange pathway.

Figure 3(c) shows the barrier heights for  $O_N$  /  $V_O$  defect exchange pathways. It is evident that such defects are likely to be kinetically, and not thermodynamically, limited. Notably, there is only one exchange pathway that has any real relevance at operating conditions, viz. the  $V_{01} \rightarrow O_N$  exchange. The barrier preventing this exchange ranges between ~2.1 eV for a neutral vacancy defect, to ~0.5 eV in the presence of a  $V_N^{\bullet\bullet\bullet}$  defect. This may indicate that high defect charges can rearrange in the material through multiple defect hops through low energy barrier pathways. By comparison, O<sup>2-</sup> exchange from V<sub>02</sub>, V<sub>03</sub>, V<sub>04</sub> and V<sub>05</sub> positions is kinetically similar and less favourable, with barrier heights ranging between 2.40-3.11 eV (for  $V_N^{\times}$ ) to 1.59-2.64 eV (for  $V_N^{\bullet\bullet\bullet}$ ). Exchange from V<sub>06</sub> and V<sub>07</sub> positions is unlikely, being prevented by barriers of ~3.5 – 4 eV and ~5 – 5.5 eV, respectively. Interestingly, the charge of the nitrogen vacancy defect has an opposite trend on these diffusion barriers, with the barrier heights increasing with charge state.

Pathways associated with a N<sup>3-</sup> anion diffusing into a V<sub>0</sub> defect to form an N<sub>0</sub> anti-site defect are shown in Figure 4(a). Figure 4(b) shows that the formation energies associated with this process are markedly different to those for the reverse exchange process that forms  $O_N$  anti-site defects (Figure 3(b)). N<sup>3-</sup> exchange becomes significantly less favourable with increasing vacancy charge, irrespective of the N<sup>3-</sup> ion's original position in the lattice. More interesting however is the comparison of formation energies in for neutral and singlycharged  $V_0$  defects. The analogous  $V_N$  defects had comparable formation energies (Figure 3(b)). However, Figure 4(b) shows that the increased charge in the oxygen vacancy defect makes the  $N_0$  anti-site defect up to ~1 eV less stable. This is further evidence indicating that the stability of these defects is largely determined by the vacancy location in the TaON lattice, as noted above. Diffusion barriers provided in Figure 4(c) indicate that  $N_0 / V_N$  exchange is also less dependent on the vacancy charge, compared to the trends shown in Figure 3(c) for  $O_N / V_O$ defect exchange. Exchange of the  $N^{3-}$  ion at position  $V_{N2}$  into the

#### Journal of Materials Chemistry A

oxygen vacancy defect is the most kinetically favourable, with barriers ranging between ~1.9 (for a  $V_0^{\times}$  defect) to ~1.5 eV (for  $V_0^{\bullet\bullet}$ ). Otherwise, N<sup>3-</sup> is unlikely to be competitive under а operating conditions, with barriers exceeding ~2.5 eV in the presence of neutral vacancy defects, and increasing to as much as ~4.5 eV for  $V_0^{\bullet\bullet}$  defects. Comparison of Figures 3(c) and 4(c) shows again that diffusion of O<sup>2-</sup> is the likely dominant contributor to ionic mobility arising from vacancy exchange pathways, compared to N<sup>3-</sup>. While positive charge states do not stabilise  $V_0$  defects in TaON by forming  $N_0 / V_N$  defect pairs, but instead do the opposite; i.e. increasing the positive charge on a  $V_N$  vacancy shifts an adjacent  $O^{2-}$  to form an  $O_N / V_O$  defect pair. Thus, it is likely that the vacancy exchange mechanism in neutral and charged regions of TaON will differ, due to the relative stabilities and mobilities of  $O_N / V_O$  and  $N_O / V_N$  defect pairs.

#### $V_{N}$ Diffusion Barriers in Bulk $Ta_{3}N_{5}$

TaON and Ta<sub>3</sub>N<sub>5</sub> have both been studied as potential photocatalysts, due to their favourable band edges for visible light absorption, and more recently as a combined heterojunction.<sup>36</sup> The synthesis of these two stable stoichiometries via ammonolysis/nitridation of an oxide precursor (Ta<sub>2</sub>O<sub>5</sub>) means that these three materials have often been characterized or studied in series to investigate the tradeoff between stability and enhanced sunlight absorption afforded by nitrogen doping.3, 30, 37, 38 Notably, Ta<sub>3</sub>N<sub>5</sub> itself requires oxygen, either in the form of the oxide precursor or O<sup>2</sup> gas in magnetron sputtering synthesis, to stabilize the Ta5+ coordination environment. Without O2 in the latter technique, TaN is formed, while ammonolysis unavoidably leaves oxygen in the substrate.<sup>39, 40</sup> The stability of oxygen impurities in nitride phases is exemplified in the present context by evidence of TaON forming at Ta $_3N_5$  surfaces under catalytic conditions.<sup>35</sup> On this basis, the relative mobilities of the native N<sup>3-</sup> ions and O<sup>2-</sup> impurities exchanging with vacancy sites in bulk  $Ta_3N_5$  are considered.

Nitrogen ions in bulk Ta<sub>3</sub>N<sub>5</sub> exhibit two distinct coordination environments, and are either 3-coordinate or 4-coordinate. The 3-coordinate N's form regularly spaced channels through the bulk Ta<sub>3</sub>N<sub>5</sub> structure, evident in Figure 5. Consequently, the 3coordinate N and the 4-coordinate possess very different formation energies, as shown in previous reports.<sup>8, 27, 41</sup> Thus N<sup>3-</sup> vacancy migration has been categorized as those pathways between two 3-coordinate sites (Figure 5(a)), those between two 4-coordinate sites (Figure 5(b)), and those between a 3coordinate and 4-coordinate site (Figure 5(c)). The  $2 \times 2 \times 1$  Ta<sub>3</sub>N<sub>5</sub> supercell used here enables all potential coordination rearrangement pathways from 3- to 4- coordinate N sites to be investigated. Previous studies looking at charged point defect formation energies have focused on a 3x1x1 supercell of the non-primitive unit cell.8, 26, 27 While this bulk cell would be suitable for simulating interstitial pathways and migration between 3-coordinate sites, a wider, not deeper cell has been used here, so that coordination rearrangement pathways, rather than cavity-hopping pathways can be studied.



**Figure 5.** (a)  $V_N$  migration pathways and corresponding barrier heights in  $Ta_3N_5$  (a) between 3-coordinate  $N^{3-}$  sites, (b) between 4-coordinate  $N^{3-}$  sites and (c) between 3-coordinate and 4-coordinate  $N^{3-}$  sites. Vacancy charge is denoted using Kröger-Vink notation. Lines are provided to guide the eye. Complete NEB pathways are provided in Figure S5 & S6.

It is immediately apparent from Figure 5 that, unsurprisingly, the most labile V<sub>N</sub> vacancy diffusion in Ta<sub>3</sub>N<sub>5</sub> occurs between 3coordinate sites in the bulk lattice. There are two distinct pathways possible,  $V_{N1} \rightarrow V_{N2}$  and  $V_{N1} \rightarrow V_{N1-mirror}$  (Figure 5(a)). Both are prevented by barriers less than ~1 eV that are largely independent on the charge state of the vacancy defect. By comparison,  $V_N$  migration between 4-coordinate sites are associated with significantly higher barriers (Figure 5(c)). Diffusion between  $V_{N1}$  and  $V_{N4\text{-mirror}}$ ,  $V_{N4\text{-side}}$ ,  $V_{N5\text{-side}}$  and  $V_{N5\text{-mirror}}$ each have similar barriers, ranging between 2.77-3.35 eV for  $V_N^{\times}$ and 2.48-3.15 eV for  $V_N^{\bullet\bullet\bullet}$ . Thus, there is little charge effect on  $V_N$  diffusion via these pathways as well. On the other hand, the shorter migration path between  $V_{N1}$  and the neighbouring  $V_{N4}$ site decreases by ~1.5 eV with increasing vacancy charge, from 2.59 eV for  $V_N$  to 1.44 eV for  $V_N^{\bullet\bullet\bullet}.$  Migration between  $V_{\text{N1}}$  and  $V_{\text{N3-mirror}}$  vacancy sites corresponds to a cavity-jumping path, and consequently has a larger migration barrier of ~4.5 eV. This is comparable to barriers observed for V<sub>N</sub> diffusion between 4coordinate sites, which are provided in Figure 5(b). The migration of N<sup>3-</sup> vacancy defects between V<sub>N4</sub> and V<sub>N4-side</sub> / V<sub>N5-</sub>  $_{side}$  sites are lower in energy than those for  $V_{N3}$  and  $V_{N5}$  by a significant margin; by up to ~2 eV for neutral vacancies, and more than 3 eV for  $V_N^{\bullet\bullet\bullet}$  defects. This is somewhat counterintuitive, since although the  $V_{\text{N3}}$  and  $V_{\text{N5}}$  sites are further from the original  $V_{N4}$  site, they are also less crowded by  $Ta^{5+}$ ions. Further, the 'more crowded' local migration paths between Ta<sup>5+</sup> ions around 4-coordinate N's are predicted to have lower migration energy barriers with increasing vacancy

#### ARTICLE

charge state, whereas the opposite is true for the paths between coordinating sites on  $Ta^{5+}$  ions adjacent to the channel.

#### Oxygen Impurity Diffusion in Bulk Ta<sub>3</sub>N<sub>5</sub>

Oxygen impurities in  $Ta_3N_5$  are known to have a significant impact on charge recombination and have been suggested to be the origin of limited photocatalytic performance for this material.<sup>35, 42</sup> Because of this issue, protective layers or shells such as  $Cr_2O_3^{43}$  or  $MgO^{44}$  have recently been used to coat  $Ta_3N_5$ photoabsorbers in electrochemical cells to insulate them from degradation and improve device stability.

Considering the relative diffusion kinetics established above for TaON, it is anticipated that the presence of oxygen impurities in Ta<sub>3</sub>N<sub>5</sub> will likely dominate this material's ionic mobility. Comparison of Figure 5 and 6 shows that this is the case. Figure 6 depicts the possible exchange pathways of  $O_N / V_N$  impurity defect pairs in bulk  $Ta_3N_5$  and the corresponding migration energy barriers. Because an  $O_N$  impurity can be modelled in the 0 / +1 state, migration barriers of defects comprising a hole on the  $O_N^{\scriptscriptstyle\bullet}$  anti-site defect and a  $V_N^{\scriptscriptstyle\bullet\bullet\bullet}$  vacancy have been included in the discussion here. Figure 6(a) shows that diffusion of  $O_N$ defect between 3-coordinate N<sup>3-</sup> sites is prevented by barriers as low as ~0.4 eV. These are therefore the dominant diffusion pathways for oxygen impurity defects in Ta<sub>3</sub>N<sub>5</sub>. Interestingly however, barrier heights increase to a maximum between 0.7-0.97 eV for  $V_N^{\bullet\bullet}+O_N$  (or  $V_N^{\bullet}+O_N^{\bullet}$ ) defect pairs, before decreasing to 0.46-0.89 eV for the  $V_N^{\bullet\bullet\bullet} {+} O_N^{\bullet}$  defect combination. These barriers are consistently ~0.2-0.3 eV lower than the corresponding  $V_N$  diffusion barriers, meaning that diffusion of oxygen impurities in Ta<sub>3</sub>N<sub>5</sub> is more facile, as anticipated. The migration of oxygen impurities between 4-coordinate N<sup>3-</sup> sites is shown in Figure 6(b). Interestingly, these diffusion barriers exhibit the same dependence on vacancy charge state as observed in Figure 6(a), albeit more dramatically. They are also consistent with the trends in V<sub>N</sub> diffusion barriers in bulk TaON, shown in Figure 3(b).

The relative diffusion barriers for these oxygen impurities are also qualitatively similar to the analogous  $V_N$  diffusion barriers shown in Figure 5(b). However, the oxygen impurity diffusion barriers are again lower in most cases. This is also the case for  $O_N\,/\,V_N$  defect pair exchange between the 3-coordinate  $N^{3\text{-}}$  sites shown in Figure 6(c). However, increasing the charge state of the vacancy defect in this case consistently increases diffusion energy barriers. Thus, comparison of Figures 5 and 6 shows that the most mobile diffusion pathway in  $Ta_3N_5$  is the movement of oxygen impurities via the channel of 3-coordinate N<sup>3-</sup> sites; such  $O_N / V_N$  exchange is prevented by a lower energy barrier than that for  $V_{\text{N}}$  diffusion itself. This comparison also shows that it is significantly easier for a  $V_N$  defect to penetrate the 4-coordinate N<sup>3-</sup> network layers via exchange with an oxygen impurity, and vice versa. This trend is only reversed at higher positive vacancy charge states (i.e.  $V_N^{\bullet\bullet\bullet}$  and  $V_N^{\bullet\bullet\bullet}$ + $O_N^{\bullet}$ ).



Figure 6. (a) Ta<sub>3</sub>N<sub>5</sub> migration barrier heights associated with an O<sub>N</sub> defect exchanging with V<sub>N</sub> site (a) between 3-coordinate N sites, (b) between 4-coordinate N sites and (c) from 3-coordinate N site to 4-coordinate N site. Vacancy charge is denoted using Kröger-Vink notation. Lines are provided to guide the eye. Complete NEB pathways are provided in Figure S7 & S8.

#### Conclusions

The competing stability and migration of between O and N anion vacancy defects in the archetypal (oxy)nitride materials TaON and Ta<sub>3</sub>N<sub>5</sub> as a function of the vacancy charge state has been investigated in this work. The first-principles calculations reported here show how the local Ta<sup>5+</sup> coordination environment, vacancy defect charge and the anion coordination number each influence the dominant ionic diffusion mechanism in these materials. For vacancy diffusion in TaON, our results show that  $V_N$  migration barriers are more sensitive to the vacancy charge state, compared to the diffusion of V<sub>0</sub> defects. O<sup>2-</sup> diffusion is the likely dominant contributor to ionic mobility in TaON, consistent with previous results for YZrON.<sup>10</sup> However, it is predicted that the dominant contiributor to ionic mobility in TaON switches from O2- anion diffusion in regions of neutral/low charge, to  $N^{3-}$  anion diffusion in regions of high charge, such as electrode/catalytic interfaces. This potentially explains the experimentally-observed nitrogen deficient (001) surfaces in this material, and related oxynitrides. Further, formation of O<sub>N</sub> anti-site defects is predicted to be spontaneous in the presence of sufficiently charged  $V_N$  vacancy defects, which is consistent with the propensity of TaON to undergo oxidative decomposition, reforming Ta<sub>2</sub>O<sub>5</sub>. Similarly, migration of oxygen impurities in  $Ta_3N_5$  is shown to have lower energy barriers than nitrogen vacancies themselves. However, the influence of the charge state here is not uniform, with the nominal coordination number of  $V_{\text{\tiny N}}$  defect sites playing a significant role. It is believed that the fundamental insights into

#### Journal of Materials Chemistry A

defect formation and migration presented here provide a basis for new potential avenues by which nitrogen content in oxynitride semiconductors can be stabilised for enhanced catalytic performance.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### ARTICLE

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