Supporting Information

Limitations and improvement strategies for early transition-metal nitrides as competitive catalysts towards the oxygen reduction reaction

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Atomic %	$V_{0.95}M_{0.05}N$ (The theoretical value of M/V is 5.3%)								
	M=Ti	M=Cr	M=Mn	M=Fe	M=Co	M=Ni	M=Cu		
M/V	5.2 \pm 0.2	5.2 \pm 0.1	5.4 \pm 0.2	5.3 \pm 0.1	5.2 \pm 0.2	5.1 \pm 0.2	5.2 \pm 0.2		
S2									

(b)

O2-N2

0.2

0.4

0.6

Potential (V vs. RHE)

0.8

After 10 cycles 10mV/s 1600rpm

0.1 M KOH solution

VN M=Cu M=Ni M=Co

M=Fe M=Mn

M=Cr M=Ti

1.0

JM 20% Pt/C

1.2

0

-2

-3

-4

-5

-6

Current density (mA cm⁻²)

Table S1. EDX profile of $V_{0.95}M_{0.05}N$ obtained from three different areas.



Fig. S1. Linear sweep voltammetry curves of VN and $V_{0.95}M_{0.05}Ns$ after 10 cycles in (a) 0.1 M HClO₄ solution and (b) 0.1 M KOH solution (calculated by subtracting N₂-saturated solution from O₂-saturated solution at the rotation speed of 1600 rpm); (c) Catalytic stability of $V_{0.95}Co_{0.05}N$ and JM 20% Pt/C catalyst polarized at 0.621 V (vs RHE) during 30000 s in O₂-saturated 0.1 M KOH solution at a rotation rate of 900 rpm.



Fig. S2. Linear sweep voltammetry curves (a) and XRD patterns (b) of $V_{1-x}Co_xN$ annealed at 650°C; Linear sweep voltammetry curves (c) and XRD patterns (d) of $V_{0.95}Co_{0.05}N$ annealed at different temperature.

In order to see whether the ORR activity of VCoN can be further enhanced, we investigated the effects of Co doping amount and annealing temperature. As shown in Fig. S2(b), VCoN reached the best activity with a 5% doping amount of Co. And the metallic Co phase was observed clearly when the doping amount of Co reached 20%, as shown in Fig. S2(a). It can be noted in Fig. S2(c) that an annealing temperature higher than 550°C was needed to form VN completely. And $V_{0.95}Co_{0.05}N$ annealed at 650°C reached the best activity, as shown in Fig. S2(d).



Fig. S3. Fine XRD patterns of VN and $V_{0.95}M_{0.05}Ns$ (M = Ti, Cr, Mn, Fe, Co, Ni, Cu) obtained through a slow scanning rate (a) and the corresponding calculated lattice distortion and crystallite size (b): in the equation, $\Delta d(200)$ represents the lattice distortion according to the (200) facet, *a* and *a*' represent the lattice constants of VN and $V_{0.95}M_{0.05}Ns$, respectively.

Through the fine XRD patterns in Fig. S3(a) we can notice that the main peak (200) appeared a positive shift in $V_{0.95}T_{0.05}N$ and a negative shift in other $V_{0.95}M_{0.05}Ns$ with respect to VN. Accordingly, the calculated results in Fig. S3(b) show that doping Ti into the VN resulted in lattice contraction while doping other metals resulted in lattice extension, and the biggest lattice extension was reached by doping Fe. We may find that the lattice distortion trend has poor correlation with the atomic radius and the electronegativity of the doped metals, but it has some connection with their the d-electron numbers, which is: doping metal with less d-electrons than V led lattice contraction, and doping metal with more d-electrons than V led lattice extension. In addition, the crystallite size calculated by the Scherrer equation based on (200) facet also has a certain similarity with the lattice distortion trend, for example, the biggest lattice extension corresponds the biggest crystallite size. The doping effects on lattice distortion and crystallite size are related to the elastic property which is beyond the scope of this paper, readers who are interested in this topic are recommended to read reference.¹

Atomic %	$V_{0.95}M_{0.05}N$							
	VN	M=Ti	M=Cr	M=Mn	M=Fe	M=Co	M=Ni	M=Cu
Ν	30.09	28.03	28.38	22.48	25.57	29.42	28.63	23.69
0	22.49	23.68	23.98	26.49	24.81	19.52	20.05	27.04
V	23.94	22.36	22.63	20.88	21.61	22.37	23.19	20.33
М		2.16	2.02	5.07	3.13	3.9	3.42	3.62
V + M		24.52	24.65	25.95	24.74	26.27	26.61	23.95
M/V		9.7	8.9	24.3	14.5	17.4	14.7	17.8
The theoretical value of M/V is 5.3%								

Table S2. Atomic contents of VN and $V_{0.95}M_{0.05}Ns$ in XPS analysis.

All atoms, except C that is not derived from the catalysts, detected in XPS analysis are listed in Table S2. Clearly, the actual ratio of M/V in all $V_{0.95}M_{0.05}Ns$ is higher than the theoretical value. This deviation suggests the surface enrichment of doping metals in $V_{0.95}M_{0.05}Ns$ nanoparticles. The presence of O atoms is because the catalysts were exposed in the air for a while. Assuming all the O atoms are surface adsorbed oxygen on metal atoms, then the ratio of O/(V+M) should be close to or less than 1. However, the ratio of O/(V+M) in $V_{0.95}Mn_{0.05}N$ and $V_{0.95}Cu_{0.05}N$ is clearly higher than 1, indicating that there may exist metal oxides in them.



Fig. S4. XPS spectra of M2p in $V_{0.95}M_{0.05}Ns$ (M = Ti, Cr, Mn, Fe, Co, Ni, Cu).

For $V_{0.95}Ti_{0.05}N$, the spectrum revealed the existence of Ti^{4+} . For $V_{0.95}Cr_{0.05}N$, the spectrum revealed the coexistence of Cr^{3+} and Cr^{6+} with Cr^{3+} holding major proportion. For $V_{0.95}Mn_{0.05}N$, the spectrum revealed the coexistence of Mn^{2+} and Mn^{4+} with nearly equal proportion. For $V_{0.95}Fe_{0.05}N$, the spectrum revealed the existence of Fe^{3+} . For $V_{0.95}Co_{0.05}N$, the peaks at 780.6 eV and 782.6 eV correspond to Co^{2+} and Co-N bond, respectively. For $V_{0.95}Ni_{0.05}N$, the peaks at 853.4 eV, 855.9 eV and 857.8 eV correspond to metallic Ni, Ni²⁺ and Ni-N bond, respectively. For $V_{0.95}Cu_{0.05}N$, the peaks at 932.1 eV, 933.1 eV and 935.0 eV correspond to metallic Cu, Cu^{2+} and Cu-N bond, respectively.

S7



Fig. S5. XPS spectra of N1s in VN and $V_{0.95}M_{0.05}Ns$.

The N1s spectra were divided into four valence states: N1 (401.8 eV), N2(399.9 eV), N3 (397.4 eV) and N4 (396.6 eV).

N1 and N2 may be related to oxidized N, while N3 and N4 are associated with metal nitrides. It should be noted that different from N3 which corresponds to V-N bond and exists in all $V_{0.95}M_{0.05}Ns$, N4 was only observed in $V_{0.95}Co_{0.05}N$, $V_{0.95}Ni_{0.05}N$ and $V_{0.95}Cu_{0.05}N$, implying that N4 is related to the Co-N bond, Ni-N bond and Cu-N bond observed in Fig. S4(e-g).

S8



Fig. S6. XRD pattern of VN after the O₂-TPD test.

S9





Fig. S7 CV curves of $V_{0.95}M_{0.05}Ns$ during 10 cycles in N₂-saturated 0.1 M KOH solution, recorded at 50 mV/s without rotation.

It can be seen that VN has good stability in alkaline solution, and its stability is barely affected by the doping of Ti, Cr, Fe, Co and Ni. However, the stability of VN decreases with the doping of Mn and Cu. This is probably why the ORR activity of $V_{0.95}Mn_{0.05}N$ and $V_{0.95}Cu_{0.05}N$ showed an evident decrease after 10 cycles. In addition, additional peaks can be observed after Mn-, Ni- and Cu-doping. This may be related to the new formed species induced by these elements.

S10





Fig. S8 CV curves of $V_{0.95}M_{0.05}Ns$ during 10 cycles in N₂-saturated 0.1 M HClO₄ solution, recorded at 50 mV/s without rotation.

It can be seen that VN has poor stability in acidic solution, and its stability can only be improved by the doping Ti and Ni. This explains why the ORR activity of $V_{0.95}Co_{0.05}N$ showed an evident decrease after 10 cycles.

S11

Table S3. BET surface area of $V_{0.95}M_{0.05}Ns$.

BET surface area of $V_{0.95}M_{0.05}N$ (m ² /g)								
VN	M=Ti	M=Cr	M=Mn	M=Fe	M=Co	M=Ni	M=Cu	
12.72	15.2	18.39	11.09	8.89	9.24	8.4	13.06	

It can be seen that there is no correlation between the surface area and the ORR activity. This indicates the ORR activity

improvement is not derived from the variation of the surface area of the catalysts.

References:

(1) Chen, K. Y.; Zhao, L. R.; Rodgers, J.; Tse, J. S. J Phys D Appl Phys 2003, 36, 2725-2729.