Manganese Vanadium Oxide–N-Doped Reduced Graphene Oxide Composites as Oxygen Reduction and Oxygen Evolution Electro catalysts

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Supporting Information

ABSTRACT: The oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are key catalytic processes for sustainable energy technologies, such as water electrolysis or fuel cells. Here, a novel metal oxide–nanostructured carbon composite is reported, which acts as OER and ORR electro catalyst under technologically relevant conditions. A facile synthetic process allows the deposition of a molecular manganese vanadium oxide precursor, \([\text{Mn}_4\text{V}_4\text{O}_{17}(\text{OAc})_3]^{3+}\), on reduced graphene oxide. Simultaneously, the precursor is converted into insoluble nanostructured solid-state Mn–V oxide catalysts. Control of the synthetic conditions allows tuning of the electrocatalytic properties of the composites, leading to excellent and stable electrochemical reactivity. The electrocatalytic ORR and OER activity was evaluated in alkaline aqueous electrolyte and showed performance comparable with commercial Pt/C electro catalysts. The study thus demonstrates how polyoxometalate precursors based on earth-abundant elements can be deposited on nanostructured carbon to give high-performance OER/ORR catalysts for alkaline water electrolysis. A new class of composite catalysts can in future be accessed by a facile fabrication route.

KEYWORDS: reduced graphene oxide, polyoxometalate, oxygen reduction reaction, oxygen evolution reaction, bifunctional electro catalysts

1. INTRODUCTION

The development of sustainable energy technologies, such as water electrolysis,† metal–air batteries,‡§ and fuel cells¶ relies on earth abundant catalysts, which efficiently catalyze the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER).‡§ To this end, 3d transition metal oxides are ideal catalyst candidates, as they combine earth abundant elements with high catalytic performance, facile synthesis, and high stability under harsh chemical conditions. In particular, manganese oxides have attracted significant interest as ORR and OER electro catalysts because of their low cost, earth-abundance, low toxicity, good cycling stability, and catalytic activity.\textsuperscript{9–14} Currently, the development of this materials class is hampered by their large band gaps, leading to low intrinsic electrical conductivity. In addition, material stability and catalytic performance are key properties, which require further optimization. To this end, new mixed-metal oxides were designed to improve the ORR/OER performance, leading to 3d metal-based catalysts such as MnCo_2O_4,\textsuperscript{15,16} MnFe_2O_4,\textsuperscript{17} or CoFe_2O_4.\textsuperscript{18} Often, these materials were synthesized by thermal decomposition of two separate compounds, which give little control over the final material composition, morphology, and chemical structure. Thus, facile and efficient fabrication routes for mixed-metal oxide catalysts are still a major challenge in materials chemistry.

One promising precursor class are molecular metal oxides—so-called polyoxometalates (POMs). POMs are a family of early transition metal (TM)-oxo clusters widely used as electro catalysts for challenging reactions including the ORR and OER.\textsuperscript{19,20} Recently, POM-derived porous nanocarbon composites, containing metal carbides, nitrides, sulﬁdes, or oxides, have attracted increasing attention in the ﬁeld of electrochemical energy conversion and storage.\textsuperscript{20–22} Nanostructured mixed metal oxides are easily accessible by thermal decomposition when using mixed-metal-based POMs as precursors because the metal ratio in the POM precursors is...
predefined.\textsuperscript{20} We have demonstrated the feasibility of this approach recently and developed bottom-up approaches to deposit manganese vanadium oxides\textsuperscript{23} on conductive substrates, for example, nanostructured carbons.\textsuperscript{24}

Over recent years, reduced graphene oxide (rGO) has attracted significant interest as conductive catalyst support as it combines excellent conductivity, high surface area and outstanding chemical stability. Further, rGO can be modified to feature reactive surface groups (e.g., alcohols, amines), which are suitable for anchoring metal oxide catalysts, leading to a number of electrocatalytic composites.\textsuperscript{25–29} Also, N-doped nanocarbon materials, especially carbon nanotubes and graphene, have shown surprising catalytic activity for the ORR.\textsuperscript{30,31} However, the combination of catalytically active, stable metal oxide, and electrically conductive, nanostructured carbonaceous support is still a major challenge for modern materials chemistry and facile, scalable syntheses are urgently required to enable further progress in the field.

Here, we report the facile bottom-up fabrication of ORR/OER electrocatalyst composites formed by controlled deposition of molecular manganese vanadium oxide precursors on functionalized nitrogen-doped rGO substrates. The method presented combines easy, scalable synthesis with chemical tunability on the molecular level, so that in the current example, we can access a composite material based only on earth-abundant components. The resulting MnVO\textsubscript{4}@N-rGO composites demonstrate high ORR and OER activity and combine long-term stability with reactivity under technologically important conditions, so that based on this synthetic concept, a wide range of related composites becomes accessible. Tuning of elemental composition, structure and morphology of the composite can be used to tune catalytic performance and stability.

2. EXPERIMENTAL SECTION

2.1. Instrumentation. 2.1.1. High-Resolution Transmission Electron Microscopy (HRTEM). HRTEM measurements were performed with an image-side aberration corrected FEI TITAN 80–300 under an accelerating voltage of 80 kV.

2.1.2. Powder X-ray Diffraction (pXRD). Powder X-ray diffraction studies were performed on a BRUKER D8 Advance XRD unit using Cu Ka (\(\lambda = 1.54\) Å).

2.1.3. X-ray Photoelectron Spectroscopy (XPS). XPS analysis was performed on ESCALAB250 Thermo Electron Corporation equipment with an Al Ka X-ray source (1486.6 eV). The X-ray source was run at a reduced power of 150 W, and the pressure in the analysis chamber was maintained at 10–11 Pa or lower.

2.1.4. General Remarks. All chemicals were purchased from Sigma-Aldrich, ABCR or ACROS and were of reagent grade. The chemicals were used without further purification unless stated otherwise. \([\text{Mn}_4\text{V}_4\text{]}\) was prepared according to reference.\textsuperscript{13} For comparison, TEM images of the sonicated \([\text{Mn}_4\text{V}_4\text{]}\) were recorded and show dense aggregate structures formed by nanoparticles with diameters between ~10 and 40 nm (Figure S1a and b).

2.2. Synthesis of the Composite Materials. GO was dispersed in anhydrous acetonitrile (ACN). The concentration of the final GO/ACN suspension was ~1 mg/mL.

For the N-rGO synthesis, 2.21 mL of 35% aqueous NH\textsubscript{4}OH solution was added to 30 mL of GO/ACN suspension. The reaction was stirred at 80 °C for 12 h. Then, the reaction mixture was transferred to a 120 mL autoclave for hydrothermal reaction at 180 °C for 6 h, and the N-rGO was obtained. The resulting product was collected by centrifugation, washed with ethanol and dried.

To prepare the MnVO\textsubscript{4}@N-rGO composites, first, 5 mL of 0.018 mM \([\text{Mn}_4\text{V}_4\text{]}\)\textsuperscript{14} ACN solution was added into 30 mL of GO/ACN suspension (~1 mg/mL), followed by the addition of 2.21 mL of NH\textsubscript{4}OH (35% aqueous solution). The reaction was stirred at 80 °C with stirring for 12 h. Then, the reaction mixture from the first step was transferred to a 120 mL autoclave for hydrothermal reaction at 180 °C for 6 h. The resulting product was collected by centrifugation and washed with ethanol, then dried at 60 °C for 12 h. The collected solid was further heat-treated at 440 °C for 4 h (giving 1–440 or 900 °C for 1 h (giving 1–900)).

2.3. Electrochemical Studies. All electrochemical measurements were performed on an electrochemical workstation (CHI 730 E, CH Instruments, Inc. U.S.A) at room temperature using a standard three-electrode electrochemical cell. A Pt wire and an Ag/AgCl electrode in 3 M aqueous KCl were used as the counter and reference electrodes, respectively. All potentials in this study are given versus reversible hydrogen electrode (RHE). \(E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.219 + 0.059pH\), here 0.210 V is the standard potential for Ag/AgCl electrode at 25 °C. A glassy carbon rotating disk electrode (RDE) with 4.0 mm diameter and a rotating Pt ring-glassy carbon disk electrode (RRDE, disk diameter 4.0 mm; Pt ring inner diameter 6.0 mm, outer diameter 8.0 mm) were used as working electrode for evaluating the ORR and OER performance.

For all electrochemical measurements, the modified electrodes were used as working electrodes and prepared by the following method: 4 mg of the as-prepared catalyst, 20 \(\mu\)L of Nafion solution (5% w/w in water and 1-propanol, Naflon D-520, Germany) and 2 mL of ethanol were mixed by at least of 1 h of sonication to form a homogeneous ink. The catalyst ink (18.8 \(\mu\)L) was pipetted onto the surface of glassy carbon working electrode and air-dried. Unless stated otherwise, the catalyst loading was 0.3 mg cm\(^{-2}\). For comparison, a commercial Pt/C (20 wt % Pt on Vulcan carbon black from Premetek Co.) was deposited on the working electrode with the same procedure and tested for ORR and OER under identical conditions.

For the ORR measurements, the modified RDE was used as the working electrode and the experiment was performed in an O\textsubscript{2}-saturated solution using linear sweep voltammetry (LSV) at a scan rate of 10 mV s\(^{-1}\) with varying rotating speed from 400 to 1600 rpm.

To study the activity and selectivity of the catalyst for oxygen reduction, the modified RRDE was used as the working electrode and the LSV was recorded at a scan rate of 10 mV s\(^{-1}\) at 1600 rpm, and the ring potential was kept constantly at 1.45 V vs RHE.

3. RESULTS AND DISCUSSION

3.1. Composite Synthesis. Deposition of Mn–V-oxides on N-rGO was achieved as illustrated in Scheme 1. The Mn–V-oxide cluster \([\text{Mn}_4\text{V}_4\text{O}_{17}(\text{OAc})_3]^{3−}\) \((\text{Mn}_4\text{V}_4\text{)}^{14}\) was used as a molecular precursor, and was mixed with graphene oxide (GO) in acetonitrile/aqueous ammonia. The solution was heated to 80 °C for 12 h, which led to the oxidation of \([\text{Mn}_4\text{V}_4\text{]}\) and the growth of MnVO\textsubscript{4} nanoparticles on GO sheets. Then, hydrothermal treatment at 180 °C for 6 h enabled the crystallization of MnVO\textsubscript{4} and also the reduction and nitrogen-doping of GO, leading to N-doped reduced
graphene oxide (N-rGO). The solid product was separated, dried and thermally treated under Argon atmosphere at 440 °C (named 1−440) or 900 °C (named 1−900), leading to the formation of crystalline manganese vanadium oxide phases stably linked to the N-rGO.

3.2. Characterization. Initial structural characterization of the samples was carried out using powder X-ray diffraction (pXRD). Figure 1 shows the pXRD patterns of as-synthesized N-rGO and the MnVOₓ@N-rGO composites. The broad peak in the range between 22 and 28° is assigned to noncrystalline, defective N-rGO. The metal oxides present in the composites calcined at 440 and 900 °C can be indexed to Mn₂V₂O₇ (JCPDS 52-1265 in 1−440) and Mn₁.₅V₁.₅O₄ (JCPDS 3-90039 in 1−900), respectively (Figure 1). The peaks of the composites showed a slight shift toward higher diffraction angles as compared to the pristine oxides, indicating a reduced interplanar spacing, which could be due to the calcination process.

The structure and morphology of the composites was studied by high-resolution transmission electron microscopy (HRTEM). For 1−900, Figure 2a shows that spherical Mn₁.₅V₁.₅O₄ nanoparticles (average size 7−10 nm) are homogeneously distributed on wrinkled N-rGO sheets. The manganese vanadium oxide particles feature lattice fringes with spacings of 0.210, 0.258, and 0.295 nm (Figures 2 and S1c and d), which are in agreement with the (400), (311), and (220) lattice planes of Mn₁.₅V₁.₅O₄. For 1−440, HRTEM indicates crystalline manganese oxide particles with fringe spacings of 0.197 nm, 0.214 and 0.250 nm (Figures 2 and S1e and f), which are in line with the (314), (114), and (004) lattice planes of Mn₂V₂O₇. Inductively coupled plasma optical emission spectroscopy (ICP-OES) also gave a Mn/V atomic ratio of ∼1.09 for 1−440 and ∼1.10 for 1−900, which are consistent with the structural analysis. Note that all MnVOₓ particles observed by TEM are anchored to the N-rGO matrix, confirming the successful, stable linkage between metal oxide and the N-rGO substrate.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the composition and oxidation states of the composites. XPS spectra of both composites (Figure S2) confirm the presence of Mn, V, C, and N. As shown in Figure 3a and c, both 1−440 and 1−900 feature manganese centers in oxidation state Mn²⁺, Mn³⁺, and Mn⁴⁺. This is in line with the previously reported data for Mn₂V₂O₇ (JCPDS 52-1265) and Mn₁.₅V₁.₅O₄ (JCPDS 39-0039) and highlights the mixed-oxidation-states of both manganese oxides. In detail, for 1−440, the Mn 2p 3/2 can be deconvoluted into three peaks (640.1, 641.6, and 643.3 eV), originating from the +2, +3, and +4 oxidation states of Mn in the surface of the composite, respectively.34−36 Similar spectral features are also observed for 1−900. The Mn 3s spectra (Figure S2a and d) for both 1−440 and 1−900 show Mn 3s exchange splitting (a well-known effect in transition metals which is a sensitive probe of the local magnetic moment) of 6.20 and 6.03 eV further confirming the coexistence of Mn species in oxidation states Mn²⁺, Mn³⁺, and Mn⁴⁺.34−36 Notably, mixed-oxidation state manganese compounds have previously been proposed as highly active ORR and OER electrocatalysts.36−38 For both 1−440 and 1−900 (Figure 3b and d), the vanadium XPS spectra can be deconvoluted into contributions from V⁴⁺ and V⁵⁺, indicating that vanadium is also present in mixed oxidation states.39 Analysis of the N 1s spectra (see Figure S2b and e) for both composites indicates the presence of pyridinic N, pyrrolic N,
quaternary N, and oxidized N, respectively. Note that previous reports highlighted the importance of pyridinic and quaternary nitrogen as active sites for the ORR, so that in future, tuning of the composites could allow the further optimization of the ORR reactivity. Closer inspection shows that 1–900 features significantly less pyrrolic N but more quaternary N compared with 1–440, indicating that the calcination procedure can be used to tune the chemical nitrogen environment within the composites. Further, in both composites, the C 1s spectra (see Figure S2c and f) indicate the presence of C−/C/C═C, C−N, and C−O species and are in line with previous reports on related compounds, supporting the presence of N-doped rGO as support material. For 1−900, we note a decreased intensity of C−O and disappearance of the C═C signal (compared to 1−440), indicating that most of the oxidized C functionalities can be removed by calcination, leading to rGO with improved electronic conductivity, which is in line with recent literature reports.

3.3. ORR Activity. The electrocatalytic performance of the MnVO4@N-rGO composites was evaluated by ORR polarization curves using RDE measurements in O2-saturated 0.1 M aqueous KOH solution. Figure 4a and c shows the corresponding LSVs. For both 1−440 and 1−900, the current densities increase with increasing rotation rates, which is due to the faster mass transport on the electrode surface. The limiting current densities observed (at 1600 rpm) were 5.3 (1−440) and 4.5 mA cm−2 (1−900), respectively. The onset potential (Eonset) and half-wave potential (E1/2) of 1−900 (Eonset = 1.14 V, E1/2 = 0.80 V) are significantly more positive than the corresponding values for 1−440 (Eonset = 0.98 V, E1/2 = 0.66 V) and the nonmodified N-rGO reference (Eonset = 0.800 V, E1/2 = 0.39 V, Figure S3a), indicating the superior catalytic activity of the composite containing Mn1.5V1.5O4 as catalyst (also see Tables 1 and S1 for more details). For comparison, we also performed the ORR for native {Mn4V4} deposited on a glassy carbon electrode. However, for this system, we observed very poor catalytic activity, and more negative onset potentials and significantly lower current density were noted (Figure S4a). This emphasizes the importance of proper electrical “wiring” of the metal oxide and nanostructured carbon for improved charge transfer and resulting catalytic reactivity.

Next, we determined the electron transfer number n via the Koutecky−Levich equation. This allows us to rationalize whether the catalysts operate by a two-step two-electron or one-step four-electron O2 reduction. For nonmodified N-rGO and the native {Mn4V4} (Figures S3b and S4b), we observed electron transfer numbers of ~2−3 at all potentials studied, indicating that the oxygen reduction proceeded by two consecutive two-electron processes and the formation of hydrogen peroxide (HO2−) as intermediate. In contrast, both 1−440 and 1−900 composites show electron transfer numbers of ~4 at potentials between 0.5 and 0.7 V (Figure 4b and d), suggesting an efficient four-electron transfer pathway in ORR catalysis with no peroxide formation. This is critical for the long-term stability of the catalyst, as peroxides are often degrading the catalytic device. Thus, catalyst stability was explored by performing chronoamperometry (CA) for 1−900 (E = 0.7 V vs. RHE) in 0.1 M aqueous KOH with RDE as working electrode. As shown in Figure S5a, no significant changes in current density were observed over a period of 4 h, indicating the high durability of the composite during ORR. Further, similar CVs of 1−900 are observed before and after CA (Figure S5b), illustrating that no major electrochemical changes are observed during the long-term CA test.

Next, we used RRDE measurements to record LSV data to compare the electrocatalytic ORR performance of the composites with a commercial Pt/C electrocatalyst. Figure 5a shows the ring and disk currents recorded by RRDE at 1600 rpm in 0.1 M aqueous KOH electrolyte for 1−440, 1−900, and commercial Pt/C as a reference. The terminal disk currents produced by the composites were close to that of Pt/C, showing similar performance. Small ring currents indicate

![Figure 4. Linear sweep voltammograms (LSV) recorded by RDE in O2-saturated 0.1 M aqueous KOH solution at different rotation rates for 1−440 (a) and 1−900 (c). Panels b and d show Koutecky−Levich plots of J1 versus ω−1/2 for the corresponding 1−440 and 1−900 at different electrode potentials, respectively.](image)

![Figure 5. (a) Rotating ring−disk electrode voltammograms of 1−440 and 1−900 compared with commercial Pt/C. Conditions: O2-saturated 0.1 M aqueous KOH at 1600 rpm. The disk potential was scanned at 10 mV/s and the ring potential was kept constant at 1.45 V vs RHE. (b) Hydroperoxide formation (as percentage of total oxygen reduction products) and electron transfer number n for 1−900, 1−440, and Pt/C at various potentials based on the corresponding RRDE data in panel a. Catalyst loading amount was 0.3 mg cm−2 for all samples.](image)

Table 1. ORR and OER Performance of the Composites Studied

<table>
<thead>
<tr>
<th>composite</th>
<th>E_{ORR} at J = 3 mA cm⁻² (V vs RHE)</th>
<th>E_{ORR} at J = 10 mA cm⁻² (V vs RHE)</th>
<th>ΔE_{OER,ORR} (V vs RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1−440</td>
<td>1.67</td>
<td>2.00</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>1−900</td>
<td>1.65</td>
<td>1.85</td>
<td>1.01</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1.81</td>
<td>&gt;2.00</td>
<td>&gt;1.2</td>
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that only small amounts (<10%) of the nondesired hydroperoxides are formed, providing further evidence for the efficient four-electron $O_2$ reduction pathway by the composites. $1-900$ showed the highest electrocatalytic ORR activity with a onset potential of 1.13 V vs RHE, while $1-440$ and commercial Pt/C had more negative onset potentials of 0.99 and 0.96 V vs RHE, respectively. Note that the calculated electron transfer number $n$ for all three materials was $\sim 3.9$, which suggests a four-electron reduction. Figure 6 shows the corresponding Tafel plots where Tafel slopes of 130.9 (1–900), 66.6 (1–440), and 85.4 mV dec$^{-1}$ (Pt/C) were determined.

In sum, these analyses confirm the excellent electrocatalytic activity and stability of the composites and highlight how facile materials design based on molecular earth-abundant materials can be used to develop novel, technologically relevant electrocatalyst composites.

### 3.4. OER Activity

Next, we analyzed the OER activity of the composites. To this end, $1-440$ and $1-900$ were deposited on carbon fiber paper (CFP), and LVS analyses were performed in 0.1 M aqueous KOH (Figure 6a). The oxygen evolution potential at a current density of $J = 10$ mA cm$^{-2}$ was used as established standard for comparison of catalytic activity. Both composites show good catalytic activity with OER potentials of 1.67 V (1–440) and 1.65 V (1–900), which are comparable to recently published high-performance catalysts (see Table S1). As shown in Figure S7a, LSVs of 1–900 were recorded before and after electrochemical cycling. We observed a positive potential shift of $\sim 25$ mV (at $J = 10$ mA cm$^{-2}$) after 1500 cycles. This minor change highlights the high stability of the composite during OER. Furthermore, CVs of 1–900 before and after potential cycles (Figure S7b) are virtually identical and further support the promising long-term stability of the composite. While the Tafel slopes were 271 and 286 mV for 1–900 and 1–440, respectively, highlighting that further materials design is required to optimize OER performance of the composites (see Figure 6b). For comparison, the Pt/C reference was also examined and showed low activity with significantly larger overpotential (but lower Tafel slope) than the composites. As reference, we compared the OER performance of native N-rGO and native (Mn$_4$V$_4$)$_x$, both deposited on glassy carbon electrodes. For both references, we observed lower OER activity, thus providing further evidence for the superior catalytic performance of the composite (see Figure S8). To gain further insight into the different electrocatalytic activities of 1–440 and 1–900, we performed electrochemical impedance spectrometry (EIS) of the composites, see SI, Figure S9. Lower impedance was observed for 1–900 compared with 1–440, so that the improved electronic conductivity of 1–900 could be one reason for the higher electrocatalytic performance of this composite.

Examination of the potential difference ($\Delta E_{\text{OER-ORR}}$) between the OER potential (at $J = 10$ mA cm$^{-2}$) and the ORR potential (at $J = -3$ mA cm$^{-2}$) provides an evaluation of the overall oxygen electrode activity, and small $\Delta E_{\text{OER-ORR}}$ values are desired for optimum reversible oxygen electrode performance. The comparison shows that 1–900 features the lowest potential difference (0.85 V) of the OER/ORR catalysts examined (Table 1). The values observed for 1–900 are comparable to noble-metal-based bifunctional OER/ORR catalyst models, such as Ir/C (0.92 V), Ru/C (1.01 V), and also many nonprecious metal-based bifunctional OER/ORR catalysts. For comprehensive comparison, see Table S1.

### 4. CONCLUSION

In summary, we report a facile synthetic route leading to highly active ORR/OER electrocatalysts with performance comparable to noble-metal-based systems. Deposition of a molecular manganese vanadium oxide precursor on graphene oxide and thermal annealing gives access to nanoparticulate Mn–V–oxides stably linked to high surface-area nitrogen-doped reduced graphene oxide. Two different crystalline Mn–V oxide phases can be accessed, both of which show promising ORR reactivity and high long-term stability even under harsh electrocatalytic conditions. Both catalysts also feature promising OER reactivity and show virtually identical overpotentials, highlighting that the reactivity limitation is most likely not related to the structural features of the catalyst.

Future work will explore in details the interfacial electron transfer within the compounds to establish limitations and means for materials optimization. This could allow us to explore the use of these systems under technological conditions with a focus on water electrolysis and fuel cells.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b16578.

For materials, instrumentation, characterization, synthetic, and electrocatalytic details (PDF)

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**Author Contributions**
X.X. and R.L. contributed equally to this work. X.X. performed materials synthesis and characterization. X.X. and R.L. performed the electrochemical and electrocatalytic tests. K.C. performed the electrochemical and electrocatalytic tests. K.C. and U.K. performed TEM analyses. All authors cowrote the manuscript. All authors have given approval to the final version of the manuscript.

**Notes**

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