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# In situ growth of Pt<sub>3</sub>Ni nanoparticles on A-site deficient perovskite with enhanced activity for oxygen reduction reaction

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A novel A-site deficient perovskite  $La_{0.9}Mn_{0.9}Pt_{0.075}Ni_{0.025}O_{3-\delta}$  is developed as a catalyst for oxygen reduction reaction in alkaline solution. Pt<sub>3</sub>Ni nanoparticles are exsolved *in situ* on the surface upon reduction. The catalytic activity improves significantly after exsolution. This improvement is attributed to the synergy between the host perovskite and the nanoparticles.

The sluggish activity of oxygen reduction reaction (ORR) is a critical bottleneck of numerous electrochemical devices, such as fuel cells and metal-air batteries.<sup>1, 2</sup> To improve the efficiency of these devices, tremendous research efforts have been devoted to the development of efficient and cost-effective oxygen catalysts. Among such catalysts, perovskite oxides (with nominal chemical formula  $ABO_3$ , where A is an alkaline earth metal or rare earth metal and B is a transition metal) have shown great potential due to their compositional flexibility, structural stability, relative low cost, and high area-specific activity.<sup>3, 4</sup> However, the measured activity of perovskite oxides is still inferior to state-of-the-art precious metal-based catalysts.<sup>5</sup> Scientists have found that the performance of perovskites in solid oxide cells can be greatly enhanced by decorating their surface with catalytic metal nanoparticles.<sup>6-9</sup> Recent studies have shown that substituting transition metals (M) into the B-site of a perovskite with a moderate A-site deficiency  $(A_{1-x}B_{1-y}M_yO_3)$  can facilitate the in situ exsolution of metal nanoparticles.<sup>10, 11</sup> Numerous materials have been developed following this strategy, where exsolution ultimately leads to an improved activity.<sup>11-15</sup> However, perovskites decorated with either infiltrated or exsolved metal nanoparticles have been little used as room-temperature oxygen catalysts.<sup>16-18</sup> The goal of this article is to bridge this gap by designing a novel and active oxygen catalyst utilizing this promising approach.

We developed a novel LaMnO<sub>3</sub> (LMO)-based material with the chemical formula  $La_{0.9}Mn_{0.9}Pt_{0.075}Ni_{0.025}O_{3-\delta}$  (LMPN). LMPN is capable of exsolving Pt<sub>3</sub>Ni alloy nanoparticles upon reduction in hydrogen and its ORR catalytic activity increases significantly after nanoparticle egress. We chose LMO as the parent material due to its relatively good catalytic activity<sup>19</sup> and stability upon reduction.<sup>20</sup> The Pt/Ni molar ratios were set at 3:1 in order to promote the formation of highly active Pt<sub>3</sub>Ni nanoparticles.<sup>21</sup> LMPN was first synthesized via the sol-gel method and then reduced in H<sub>2</sub> at 500°C for 30 min in order to promote the formation of nanoparticles. Experimental details are given in the electronic supplementary information. The resulting material is called Pt<sub>3</sub>Ni/rLMPN where '/' indicates 'exsolved on' and 'r' means 'reduced'. Pt<sub>3</sub>Ni bimetallic alloy nanoparticles are shown to egress directly from the bulk of the material during reduction (Figure 1a). The nanoparticles grow evenly on the surface as protrusions attached to the host material with an average diameter of ~20 nm, as shown by the scanning electron microscopy (SEM) images (Figure 1b and Figure S1). During reduction, the material undergoes a structural phase change (Figure 1c). The X-ray diffraction (XRD) refinements of LMPN (Figure 1d) and Pt<sub>3</sub>Ni/rLMPN (Figure 1e) suggest that the lattice's structures transform from being rhombohedral (PDF 01-073-8342) to orthorhombic (PDF 01-087-2014).22, 23 More importantly, the refinement reveals the emergence, upon reduction, of an additional cubic phase (PDF 96-101-1114, space group F*m-3m,* lattice parameter a = 3.88 Å) with an ~8% area ratio, suggesting the formation of a new phase, i.e., Pt<sub>3</sub>Ni metal. Elemental analysis based on X-ray photoelectron spectroscopy (XPS) supports these results. The amounts of surface Pt and Ni increase after reduction, suggesting the exsolution from the bulk to the surface (Table S1). For comparison, we also studied the Pt singly doped LMO, *i.e.*, La<sub>0.9</sub>Mn<sub>0.9</sub>Pt<sub>0.1</sub>O<sub>3-δ</sub> (LMP), as well as undoped LMO. Their reduced counterparts are named as Pt/rLMP and rLMO, respectively. The morphology of Pt/rLMP is

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**Fig. 1** (a) Schematic illustration of the exsolution process of LMPN. (b) SEM images of Pt<sub>3</sub>Ni/rLMPN. (c) Lattice structure of LMPN and Pt<sub>3</sub>Ni/rLMPN. XRD patterns and corresponding refinements of (d) LMPN and (e) Pt<sub>3</sub>Ni/rLMPN, where the x marks represent the experimental data, red lines are calculated patterns, and green lines are the residuals. The vertical bars in (d) and (e) indicate the peaks of the refined perovskite (blue) and Pt<sub>3</sub>Ni alloy (magenta) crystal structures.

similar to that of Pt<sub>3</sub>Ni/rLMPN, and small nanoparticles grown on the surface in an analogous fashion (Figure S2). An identical reduction-driven phase transition is observed for both Pt/rLMP and rLMO (Figure S3). A similar secondary phase attributable to Pt metal is also found in Pt/rLMP with a larger lattice parameter a = 3.91 Å.

We further examined the crystal structures of Pt<sub>3</sub>Ni/rLMPN and Pt/rLMP using transmission electron microscopy (TEM). Small Pt<sub>3</sub>Ni particles with a diameter of ~20 nm are embedded in the host perovskite material (Figure 2a). A magnified Pt<sub>3</sub>Ni nanoparticle with visible lattice fringes is presented in Figure 2b. The lattice parameter of the nanoparticle is examined by fast Fourier transform (FFT) and the fringes are visualized through inverse fast Fourier transform (IFFT). The plane distance for adjacent fringes is measured to be 2.18 Å, where this value is in good agreement with reported data for the (111) oriented plane of Pt<sub>3</sub>Ni (*i.e.*, 2.19 Å<sup>21</sup> and 2.2 Å<sup>24</sup>). Analogous quantities are observed for Pt/rLMP (Figure 2c and d). The plane distance is measured to be 2.22 Å, a value in accordance with the Pt (111) plane distance (2.23 Å<sup>25</sup>). We also calculated the plane distance from the lattice parameter *a* (as obtained from XRD refinement) of the secondary phases formed after exsolution. The corresponding results are calculated to be 2.24 Å for Pt<sub>3</sub>Ni/rLMPN and 2.26 Å for Pt/rLMP. These values contribute to the evidence that Pt<sub>3</sub>Ni and Pt nanoparticles form during reduction.



**Fig. 2** (a) TEM micrograph of  $Pt_3Ni/rLMPN$  where nanoparticles are visible. (b) High resolution TEM images of the  $Pt_3Ni$  nanoparticle with visible lattice fringes. The upper right inset (within the white frame) shows the FFT of the selected area, while the lower right inset (within the red circle) depicts the

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corresponding IFFT (magnified 3 times) with selected fringes. (c) and (d) analogous data for Pt/rLMP.

The ORR activity were tested with a rotating disk electrode setup in 0.1M KOH solution. The as-prepared perovskites were mixed with VXC-72 conductive carbon black (VC) at a 5:1 mass ratio to study the intrinsic activity while compensating for their poor electrical conductivity.<sup>3, 4</sup> Experimental details are given in the ESI. The ORR activity increased significantly after exsolution (Figure 3a). The onset potential shifts positively from 0.77 V vs. the reversible hydrogen electrode (RHE) for LMO to 0.92 V for Pt<sub>3</sub>Ni/rLMPN. The limiting current density of Pt<sub>3</sub>Ni/rLMPN also increases a lot and is close to that of the commercial Pt/C (5.3 mA cm<sup>-2</sup> to 5.4 mA cm<sup>-2</sup>) at 0.3 V. The specific activity is used as an indicator for the intrinsic activity, where the ORR current densities at low over potentials are normalized with the surface area of the loaded perovskites.<sup>4, 26</sup> The specific surface area of the as-synthesized perovskite samples was analyzed using the N2 adsorption/desorption isotherms (Figure S4). All the perovskites have a similar specific surface area of around 3  $\ensuremath{\mathsf{m}}^2$ g<sup>-1</sup>. The specific activity increases dramatically after exsolution, and, for Pt<sub>3</sub>Ni/rLMPN, it is 13 times higher than that of the original LMO at 0.9 V (Figure 3b). Figure 3c and 3d shows the corresponding Tafel plots and Tafel slopes. A small slope is another indicator of the high ORR kinetics after exsolution.<sup>27, 28</sup> In particular, such slope drops from 147 mV dec<sup>-1</sup> (original LMO) to 76 mV dec<sup>-1</sup> (Pt<sub>3</sub>Ni/rLMPN), a value close to that of Pt/C (61 mV dec<sup>-1</sup>),). This result further confirms that Pt<sub>3</sub>Ni/rLMPN is highly active. For comparison with literature values, the ORR catalytic activity of some commonly used perovskite-based materials are also listed in Table S2. Most of these materials exhibit a relatively low onset potentials (in the ~0.7-0.9 V range) and large Tafel slopes (~70-170 mv dec<sup>-1</sup>). These activities are inferior to  $Pt_3Ni/rLMPN$ .<sup>16-18, 29-34</sup> In addition, we also compared the stability of the most active Pt<sub>3</sub>Ni/rLMPN with commercial Pt/C (Figure S5). The onset and half-wave potentials of Pt<sub>3</sub>Ni/rLMPN drop less than ~0.03 V after 1000 cycles, while that of Pt/C drops by ~0.12 V. All of these results make Pt<sub>3</sub>Ni/rLMPN as well as its derivatives promising ORR catalysts.



**Fig. 3** (a) ORR current densities at 1600 rpm in O<sub>2</sub> saturated On1 mol L<sup>-1</sup> KOH solution with a scan rate of  $5^{-10}$  MVIS-103AG-103ABH gof ~0.4 mg cm<sup>-2</sup>. (b) Specific activity of LMO, rLMO, Pt/rLMP, and Pt<sub>3</sub>Ni/rLMPN at 0.9, 0.8, and 0.7 V vs. RHE. (c) and (d) Corresponding Tafel plots and slopes. the same color scheme is used across all panels.

The reduction has dramatically improved the ORR activity of the starting materials.<sup>6, 10, 24</sup> In particular, the superior activity of Pt<sub>3</sub>Ni/rLMPN compared with Pt/rLMP is likely due to the egress of Pt<sub>3</sub>Ni, which is catalytically more active than Pt.<sup>35</sup> However, it is not clear if this higher activity can be solely attributed to the presence of the nanoparticles or the synergy between the egressed Pt<sub>3</sub>Ni and the perovskite. In order to resolve this issue, we prepared the Pt<sub>3</sub>Ni (Figure S6) and physically mixed it with rLMO and VC with identical Pt and rLMO mass loadings as Pt<sub>3</sub>Ni/rLMPN (mass ratio 5:1 with VC). Pt<sub>3</sub>Ni shows a lower activity than Pt<sub>3</sub>Ni+rLMO, which is in turn inferior to Pt<sub>3</sub>Ni/rLMPN (Figure S7a). These results suggest that perovskite and Pt<sub>3</sub>Ni synergistically contribute to the ORR activity, and this effect is stronger when the Pt<sub>3</sub>Ni nanoparticles are in situ exsolved. Figure 4a shows the ORR activity of Pt<sub>3</sub>Ni/rLMPN at various rotating speeds, and the corresponding Koutecky-Levich plot is given in Figure S8. The electron transfer number is calculated to be ~3.9.28 The electron transfer numbers and peroxide (HO2<sup>-</sup>) yields of Pt3Ni/rLMPN, rLMO, Pt3Ni, and Pt<sub>3</sub>Ni+rLMO are also obtained via rotating ring-disk electrode measurement (Figure S7). The perovskite samples show a similar quasi 4-electron pathway and the reacted O2 is mainly converted into H<sub>2</sub>O. In contrast, the Pt<sub>3</sub>Ni and Pt<sub>3</sub>Ni/rLMO samples have lower electron transfer numbers and higher peroxide percentages. These results further validate the synergetic effect.<sup>36, 37</sup> The strong connection, high dispersion, and small particle size obtained from in situ growth are beneficial and effectively increase the measured activity.<sup>10, 38</sup>



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different carbon ratios at 1600 rpm. (d) Total mass activity and Pt mass activity of selected samples.

We further studied the influence of catalysts loading and the mass activity to optimize the performance and test its suitability in potential applications. The impact of perovskite loading was studied by testing the ORR activity of Pt<sub>3</sub>Ni/rLMPN+VC with different mass ratios (Figure 4b). The effect of Pt<sub>3</sub>Ni loading was investigated by doubling the amount of  $Pt_3Ni$  into perovskite. We made La<sub>0.8</sub>Mn<sub>0.8</sub>Pt<sub>0.15</sub>Ni<sub>0.05</sub>O<sub>3-δ</sub> (LMPN2), reduced it to make Pt<sub>3</sub>Ni/rLMPN2, and tested its activity (Figure 4c). We normalized the kinetic current densities measured at 0.9V vs RHE with respect to the total mass of the catalyst and the mass of Pt (Figure 4d). The mass ratio of Pt versus the total catalyst loading is calculated from the stoichiometry of the formula, *i.e.*, 0.06 for pure Pt<sub>3</sub>Ni/rLMPN and 0.12 for pure Pt<sub>3</sub>Ni/rLMPN2, as given in the ESI. The Pt<sub>3</sub>Ni/rLMPN+VC (1:1) has the highest total mass activity, ascribed to the improved electrical connection and surface utilization.<sup>39</sup> The total mass activity increases significantly for Pt<sub>3</sub>Ni/rLMPN2 in comparison to Pt<sub>3</sub>Ni/rLMPN, due to the higher Pt<sub>3</sub>Ni coverage (Figure S9).<sup>40</sup> In contrast, Pt<sub>3</sub>Ni/rLMPN with the carbon ratio of 1:3 has the highest Pt mass activity due to the lower loading, even higher than Pt/C. To further improve the catalytic activity of this special class of materials, more work is needed to optimally select the parent materials, exsolved metals, and doping levels. Highly active metal or metal alloy nanoparticles with smaller particle size, better dispersion, and a strong connection with the parent perovskite material may ultimately lead to improved performance over state-of-the-art catalysts.

Apart from the remarkable performance of Pt<sub>3</sub>Ni/rLMPN, the ORR activity of LMO also slightly increases after reduction (Figure 3a), possibly due to the structural transition and the reduction.<sup>41</sup> According to the XPS (Figure S10) and iodometric titration (Table S3), the average valence state of Mn decreases after reduction. It is expected that the concentration of oxygen vacancies increases consequently, positively affecting the oxygen reaction activity.<sup>26</sup> We also measured the oxygen evolution reaction (OER) activity of the materials (Figure S11). The OER activity shows a moderate improvement after reduction, and is explained using molecular orbital theory. As the surface Mn valence state drops, the e<sub>g</sub> occupancy in the Mn 3d orbital rises from 0.95 to 1.59, a value closer to the OER activity volcano peak.<sup>3</sup>

#### Conclusions

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In conclusion, we have developed an A-site deficient perovskite material LMPN and exsolved  $Pt_3Ni$  nanoparticles using *in situ* reduction. The ORR activity of  $Pt_3Ni/rLMPN$  improved dramatically after exsolution due to the synergy between the parent perovskite and the active  $Pt_3Ni$  nanoparticles. A number of novel materials with high activity towards oxygen catalysis at room temperature may be developed following a similar approach to the one undertaken in this work.

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A perovskite material with *in situ* exsolved Pt<sub>3</sub>Ni nanoparticles is applied for oxygen reduction reaction catalysis with dramatically improved activity.