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Cultivating Crystal Lattice Distortion in IrO_2 via Coupling with MnO₂ to Boost Oxygen Evolution Reaction with High Intrinsic

Activity

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Zhenhua Zhou, ^a Waqas Qamar Zaman, ^a Wei Sun, ^a Li-mei Cao, ^a Muhammad Tariq, ^a and Ji Yang ^{a,b}

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Here, we report an effective strategy to lower Ir consumption and boost OER performance in acid by loading IrO_2 onto MnO_2 , in which the IrO_2 crystals are well dispersed, and undergo a so-called z-extension Jahn-Teller distortion in the octahedral structure. Comparing with IrO_2 , the mass activity and intrinsic activity for IrO_2/MnO_2 were largely increased.

Catalysts for electrochemical processes sit at the heart of key renewable-energy technologies such as energy conversion of intermittent solar and wind into chemical fuels (H₂ via water splitting).¹ However, the anodic electrochemical processes consume large amounts of energy, which remains a bottleneck in the technologies.² For these reasons, there is growing demand to design more affordable, efficient and durable oxygen evolution reaction (OER) catalysts, and to further exploit their structure dependent properties. Currently Ir based catalysts play important roles in electrochemistry, as quantitatively an adequate proportion of Ir is being utilized for electrochemical techniques(Figure S1).³

Strategies to design OER catalysts for acid solution show clear difference from that for alkaline.^{4, 5} Normally, a wide variety of catalysts including metal oxides, sulfides, selenides, phosphides, and metal-free catalysts, have been developed for alkaline electrolyte.⁶⁻⁹ Furthermore, the nanostructuring of catalysts and loading onto supports largely expose the active sites and enhance the OER performance.^{10, 11} These efforts realize the goal to drive OER reaction with earth-abundant transition metal alternatives instead of precious metals. Unfortunately, the hydrogen commonly generates at low efficiencies in alkaline condition.¹² On contrary, acidic electrolysis using polymer electrolyte membrane (PEM) offers

critical advantages like load flexibility, voltage efficiency, and hydrogen purity. The catalysts used in acidic conditions are mainly based on rutile type IrO_2 or RuO_2 .¹³⁻¹⁵ To save the precious metals, significant researches have been reported including introduction of dopant atoms or crystal defects, oxide surface leaching, and dispersion onto supports.¹⁶⁻¹⁸ It is worth mentioning that the lattice distortion (axis c/a contraction in $[IrO_6]$ octahedron) and robust catalyst/substrate interface ($IrNiO_x/ATO$, IrO_2/ATO) were reported as two effective approaches to simultaneously give enhancement to catalytic activity and durability performance in acid electrolyte.^{16, 17, 19} However, combining these two approaches has yet not been reported.

Mn oxides have been used as capacitor, however, underappreciated as OER catalysts.^{20, 21} Birnessite MnO₂ (Na_{0.55}Mn₂O₄•1.5H₂O, also known as δ -MnO₂) has a layered structure consisting planar edge-sharing [MnO₆] octahedra, guest cations, and H₂O molecules.²² In the synthesis of IrO₂/MnO₂ (Scheme S1, Fig S2, Table S1), the δ -MnO₂ was generated at room temperature (RT). Ir cations enabled to enter the gallery space of birnessite MnO₂ through ionic exchange, which is similar to AuCl₄ getting into layered double hydroxide (LDH) as reported previously.²³ Hydrothermal reaction led to the crystallization of IrO₂ nanoparticles and exfoliation of birnessite Mn oxide. The Ir/Mn atomic ratios revealed by EDS (Figure S3) were close to the ratios of Ir/Mn in the starting precursors.

The SEM images reveal the morphology of catalysts (Fig. 1a, b). With Mn content increasing, the morphology of particles gradually transform from nanospheres to corrugation with observable ridges (Figure S4-6). The Transmission electron microscopy (TEM) image of Ir0.3/Mn0.7 further confirms the formation of ridges, as it appears spatially coarse (Figure 1c). The ridges and interlaid flat areas may result from the mechanically weak holding power after exfoliation. In Figure 1d, the high-resolution TEM (HRTEM) image shows the characteristic lattice fringes for IrO₂. The EDS mapping shows uniform distribution of Ir and Mn (Fig. S7). The TEM images in

^{a.} State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Processes, School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237,

P. R. China

^b Shanghai Institute of Pollution Control and Ecological Security, Shanghai200092, P.R. China

⁺ yangji@ecust.edu.cn

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Figure S8 show adjoining parts of MnO_2 and IrO_2 , implying lattice mismatch happens.



Figure 1. (a) and (b) SEM images of Ir0.3/Mn0.7 at different magnifications. (c) TEM and (d) HRTEM images of Ir0.3/Mn0.7. The inset pattern in (d) is the inverse Fast Fourier Transform pattern of (d), and the line 1, 2 and 3 is directed to the crystal diffraction of MnO_2 , IrO_2 (101), and IrO_2 (110), respectively.

X-ray diffraction (XRD) patterns in Fig. 2a show an IrO2 rutile structure (JCPDS 15-0870) for all catalysts. No characteristic peaks of birnessite (Fig. S9) or other Mn related peaks were observable probably as a result of exfoliation. Note that marked peak shifts toward higher angle were observed for the peaks involving c-axis (mainly (101) and (211), Fig 2b, c). Thus, we further investigated effect of Mn on the IrO₂ rutile structure. Within a wide range of Mn content, the rutile structure was maintained. However, with increasing Mn content, the shifts associated to peaks (101) and (211) presented a linear relationship, while the peaks with absent caxis (like (110) peak) had negligible variation. The observation of XRD peaks shift nullified the Mn^{IV} doped IrO₂ situation, which has been reported previously.¹⁶ Thus we speculated that the [IrO₆] octahedron was distorted as a result of strong interaction between IrO2 and MnO2. Besides the distortion effect in the composites, the surface area and volume of pores are increased when increasing Mn from IrO₂ to Ir0.4/Mn0.6, proving the positive role of Mn oxide (Fig. S11, 12).

The Nyquist plots reveal that Ir0.4/Mn0.6 shows the lowest polarization resistance, i.e. the highest OER activity among all composites (Fig. S13, 14, Table S2). In Fig 3a and S15, the OER polarization curves from IrO₂/MnO₂ composites and the corresponding overpotentials at current density of 10 mA cm⁻² (η_{10}) are analyzed. The onset potential for Ir0.4/Mn0.6 is merely 1.437V, and η_{10} is merely 1.516V, which are 44mV and 57mV lower than commercial IrO₂ (IrO₂-c, Adamas-beta, Fig. S10), respectively (Fig S16, Table S1). The η_{10} values of Ir/Mn

composites were significantly decreased when lowering Ir content from IrO_2 to IrO.4/Mn0.6.



Figure 2. (a) XRD pattern of Ir/Mn composites. The black lines at the bottom show the diffraction angle of IrO_2 . (b) A close view of XRD pattern of peak (101). (c) The fitted curve of diffraction angle of (101) for different IrO_2/MnO_2 composites.

For all Ir/Mn composites the Tafel slope is found to be 40 mV/dec or slightly higher, indicating that the deprotonation of the reaction intermediate OH_{ads} controls the overall reaction rate (Fig. S15, Table S3, Note S1). Considering that a Tafel slope of 56 mV/dec is observed for homemade IrO₂, it can be inferred that the OER at the Ir/Mn composites is not only a kinetically faster process, but it also follows a different reaction mechanism than at bare IrO₂.

Stability of the materials was checked by chronopotentiometry measurements at a constant current density of 100mA cm⁻² (Figure 3b). As the OER proceeds, catalysts lose their activity and need higher potential to obtain the set current density. The Ir0.3/Mn0.7 and Ir0.4/Mn0.6 well retained the required potentials even after 40000 s, much more constant than IrO₂.

The mass activity related to the Iridium consumption is an important parameter, as the cost is also bottleneck issue in electrochemistry. The mass activity of Ir0.4/Mn0.6 is measured to be 66A $g_{\rm ir}^{-1}$ at 1.50V_{RHE}, showing improved mass activity compared to other Ir-containing catalysts (Fig 3c, Table S4). The Ir mass activity of Ir0.4/Mn0.6 is 22 times than that of homemade IrO₂, while the Brunauer-Emmett-Teller (BET) surface area is just 2.6 times higher, proving that the enhancement in electrochemical performance of the composite catalysts is not limited in increasing surface area.

As electrochemical surface area (ECSA) or double layer capacitance (C_{dl}) is proportional to the active sites involved in electrochemical reactions, the cyclic voltammograms (CVs) were carried out to determine the ECSA by measuring the charging currents of double-layer capacitance at different scan rates or electrochemical impedance spectroscopy (EIS) measurements (Fig S 14, 16, 17, Table S2). The C_{dl} of Ir0.4/Mn0.6 at 1.25V (CV) and 1.49V (EIS) show a similar value (about 11mF), that is about 2 times higher than that for IrO₂. By eliminating the OER current with respect to the corresponding BET surface area and ECSA at 1.49V (EIS), the normalized specific or intrinsic activity is estimated (Figure 3d, S18). The specific activity at 1.50V of Ir0.4/Mn0.6 is 23 μ A cm_{BET}⁻² and 4 μ A cm_{ECSA}⁻², which are 3.8 and 5.6 times higher than that of pure IrO₂, respectively. This reveals that coupling

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of MnO₂ enhances the catalytic performance of IrO₂. Further, estimation of the intrinsic activities were carried on by turnover frequency (TOF), assuming that every Iridium atom is catalytically active. The IrO.4/MnO.6 composite was found to exhibit the highest TOF of ~1.7 ×10⁻² s⁻¹ at 260mV overpotential. We did not count Mn considering that Mn was inactive at the given OER potential region.



Figure 3. (a) Polarization curves and (b) electrochemical stability of IrO_2/MnO_2 materials and homemade IrO_2 (IrO_2 -h) and commercial IrO_2 (IrO_2 -c) nanoparticles. (c) Ir mass activity and (d) oxide specific activity of OER catalysts in acidic electrolyte. The specific Tafel plots of IrO_2 -h and IrO.4/MnO.6 are normalized to their respective BET surface area, while IrO_2 -ref and RuO_2 -ref²⁴ are normalized to surface area estimated from particle size analysis from TEM images. Catalysts IrO.4/MnO.6, IrO_2 -c and IrO_2 -h are from this work. The IrO_2 -Ti O_2 -245,²⁵ $IrO_x/ATO,¹⁷$ IrO_2 -150,²⁶ $IrNiO_x/Meso-ATO-180,^{18}$ IrO_2 -ref, and RuO_2 -ref²⁴ catalysts are duplicated or redrawn from literature.

X-ray photoemission spectrum (XPS) reveals that the composite has plenty of surface Ir^{III}, Mn^{III} and hydroxyl oxygen defects as shown in detail in Figure S19-22. For Ir4f spectrums, the Ir0.3/Mn0.7 can be seen to have less intense peaks and more obvious asymmetry (Figure S19, Note S2), which can be ascribed to Ir^{III} electronic defects, as has been observed in amorphous IrO₂ powders.¹³

X-ray absorption measurement were further used to explore origin of the high-energy structure (Fig.4, S23-25). Synchrotron-based X-ray absorption near edge structure (XANES) spectra of Ir L_3 ($2p_{3/2}$ to 5d) adsorption edge, characterized by the white-line, provides information about the oxidation state of Ir species. As shown in Figure 4a, with decreasing Ir/Mn, the peak intensity of absorption edge enhances, indicting a slightly higher Ir oxidation when Mn

content is higher. Nevertheless, all the composites show lower intensities than IrO_2 . The decreasing in white line of Ir supports the suspicion that Ir oxidation state is slight lower than 4+. From the XANES spectra of Mn in Fig. S24, it can be seen that the composites possessed negative shifts, which corresponds to the presence of Mn^{III} species.



Figure 4. (a) The Ir L_{III}-edge XANES spectra for IrO_2/MnO_2 composites. The inset I is the white line spectra; (b) Fourier transforms of k₃- normalized Ir-L_{III} edge EXAFS. The k range is 3-14Å. The region II reflects the adsorption edge of Ir-O shell, and the region III and IV reflect the Ir-Ir shells; (c) Enlarged view of Ir-Ir shells. (d) The schematic diagram for Ir-Ir shells and crystal structure of IrO₂.

To further investigate the local geometrical structure, Extended X-ray absorption fine structure (EXAFS) spectroscopy measurements were performed (Fig. 4b and c). The peak around 1.9 Å in the R-space Fourier transforms (FTs) spectra is attributed to Ir-O interaction in the first coordination shell. The peak around R=3.1 Å is related to the Ir-Ir coordination shell (edge-sharing). As illustrated in Figure 4b and c, for a series of composites, the edge-sharing Ir-Ir shell peaks generally shift toward lower R as Ir/Mn decreases, displaying noticeable distinction in comparison with that for IrO_2 . The shortened distance reflects the reduction in crystal c-axis length, verifying the distortion in [IrO_6] octahedral unit.

As for the Fourier transform of EXAFS spectra of Mn K-edge (Figure S24), the bond lengths of both Mn-O shells (near 1.8Å) and Mn-Mn shell (near 2.8Å) of α -, β -, and δ -MnO₂ are very close. However, there is an peak at ~3.2Å of Ir0.3/Mn0.7 which may correspond to the Mn-Mn shell of α -MnO₂.²⁷ One Mn-O shell of δ -MnO₂ also shows a peak near 3.2Å, but its intensity is relatively much lower compared to the intensity of first Mn-O shell or Mn-Mn shell.^{21, 28} Thus, the Mn oxide in Ir0.3/Mn0.7 is mixture of α -MnO₂ and exfoliated δ -MnO₂,

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implying that the $\delta\text{-MnO}_2$ has partly gone through phase transformation in hydrothermal reaction.

The distortion in crystal structure is simulated by Diamond software (Table S5, Note S3), confirming a higher Mn content benefits for the Jahn-Teller distortion effect. As has been previously reported, the z-extension Jahn-Teller distortion positively effects OER performance of IrO₂. ^{16, 29, 30} For IrO₂, the electronic structure of Ir is $5d^56s^0$, and 5d electrons tend to fill the lower state t_{2g} orbitals (i.e., d_{xz} , d_{yz} and dx^2-y^2) before they occupy the upper state e_g doublet (i.e., d_{xy} and dz^2) under the octahedral crystal field. In the case of fabricated composites, the obtained curves from sum of second-derivation spectra showed discrete transitions for Ir/Mn composites, as illustrated in Figure S25, indicating partially filled eg orbitals by 5d electrons. On the basis of the d-band theory, the electrochemical OER activity of transition metal oxide is related to the interaction between oxygen p states and metal d states³¹. Electrons in e_{σ} orbital participate in σ -bonding with a surface-anion adsorbate and influence the bond strength of oxygen-related intermediate species, which moderate surfaceoxygen bond strength (neither too strong nor too weak), thus playing an important role in fostering performance and optimization³¹. MnO_x, as an added substrate along with stronger interaction also provided a larger surface area for confronting active sites of IrO2, and raised the specific activity of IrO2. These advantages of the composite are held responsible for the synergistic OER catalytic activity.

To summarize, we have provided a feasible strategy for efficient OER electrocatalysts applied in acid media. By a simple hydrothermal approach, IrO_2 is anchored on Mn oxide. The robust composites show superior OER performance. Comparing with IrO_2 , both the specific activity and mass activity for IrO.4/MnO.6 are largely increased. The IrO_2 is found to undergo a z-extension Jahn-Teller distortion and the e_g orbital is partly filled after coupling with MnO_2 . We believe that this study opens up new vision for catalyst/subtract interaction and designing for catalysts.

Conflicts of interest

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There are no conflicts to declare.

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