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Authors: Weiwei Gu, Ye Song, Jingjun Liu, and Feng Wang

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Lanthanum-Based Compounds: Electronic Bandgap-Dependent Electro-Catalytic Materials toward Oxygen Reduction Reaction

Weiwei Gu, Ye Song, Jingjun Liu,* and Feng Wang*

Abstract: The electronic energy level of lanthanum compounds plays an important role in oxygen reduction reaction (ORR) electrocatalytic process. In this work, three lanthanum compounds, LaOHCO₃, La₂O₂CO₃ and La₂O₃, were synthesized via an in-situ urea hydrolysis method, followed by annealing at different temperatures. Among these lanthanum compounds, the layerstructured La2O2CO3 has the minimum bandgap and a moderate value of conduction band (CB) and valance band (VB). Electrochemical measurements in 0.1 M KOH solution show that compared with the other catalysts, La2O2CO3 exhibits the best electro-catalytic activity with lowest H2O2 production and highest durability for ORR, which proves the close correlation between electronic energy level and electro-catalytic ORR activity. During the ORR process over La₂O₂CO₃, some covalent electrons from VB are first excited into CB and then transfer into the unoccupied π^*_{2p} orbitals of active oxygen molecular, leading to a strengthen oxygen adsorption and promoting the reduction of oxygen. Moreover, La₂O₂CO₃ has an ability of chemical disproportionation for hydrogen peroxide (HO₂), and the produced HO₂ at the energy level of O₂/HO₂ level can undergo prompt chemical disproportionation into O₂ and OH⁻ species. The generated O₂ at this stage is adsorbed on the catalyst surface, which can be utilized for further oxygen reduction again.

Introduction

Lanthanum-based compounds, such as LaOHCO₃, La₂O₃ and La₂O₂CO₃, have been widely applied in photo-catalytic and electro-catalytic fields, including methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR).^[1-3] Based on their unique electronic structures, the reasons for lanthanum-based compounds as cheap and efficient catalysts can be ascribed to two aspects. Firstly, lanthanum ions have unfilled 4f and 5d orbitals that have characteristic f-f and f-d electron configurations to form unique bonding characteristics because lanthanum ions are located in f-block.^[4-6] As a result, the fundamental bandgap of lanthanum ions through intra-atomic hybridization between the 4f orbitals and 5d orbitals via the electron transfer within lanthanum-based compounds.^[7-9]

W. Gu, Y. Song, J. Liu, F. Wang

State Key Laboratory of Chemical Resource Engineering

Beijing Key Laboratory of Electrochemical Process and Technology for Materials

Beijing University of Chemical Technology, Beijing 100029 (P.R. China)

E-mail: liujingjun@mail.buct.edu.cn,

wangf@mail.buct.edu.cn

Secondly, the energy levels of La 4f orbitals locate below the Fermi level about 5 eV, which leads to the 4f orbitals are partly delocalized and couple with the conduction band (CB) of the compounds.^[10-11] Therefore, some electrons within 4f orbitals will be able to transfer into the conduction band through the strong interaction between the localized 4f orbitals and the delocalized conduction band, which can further alter the electronic configuration of these lanthanum compounds.^[12] Such unique electronic configurations for lanthanum-based compounds may lead to their highly electro-catalytic activity toward ORR.

To date, some lanthanum-based compounds, such as LaMnO₃, La₂O₂CO₃ and La₂O₃ with highly ORR electro-catalytic activity in alkaline media have been widely investigated.^[13-15] For example, it has been reported that La₂O₃ nanoparticles covered on carbon support exhibit low hydrogen peroxide production during ORR process compared with other metal oxides. In generally, metal oxide catalysts have relative higher HO₂⁻ production ratio than precious metal catalysts (Pt/C), which should be ascribed to the complicated oxygen reduction process, where O₂ is more feasible to be reduced to HO₂⁻. In the ORR process, the oxygen reduction reaction undergoes two/four electron transfer process with following equations, with the production of OH⁻ or HO₂⁻.

$O_2 + 2H_2O + 4e^- = 4OH^-;$	$E^0 = 0.401 \text{ V vs SHE}$
$O_2 + H_2O + 2e^- = HO_2^- + OH^-;$	E ⁰ = -0.076 V vs SHE

For lanthanum-based compound, it has the ability to chemical disproportionation for hydrogen peroxide (HO2-), which can lead to the produced HO2⁻ species undergo prompt chemical disproportionation into O2 and OH species, leading to lower hydrogen peroxide production during ORR process. Besides, lanthanum-based compounds also show excellent activity in catalyzing ORR. The reason for such superior ORR electrocatalytic activity may be attributed to that La2O3 owns a moderate band gap (between 2.8 and 5.4 eV).^[16] In the ORR catalyzing process, La₂O₃ as a Lewis base tends to provide electrons, which can facilitate the sluggish ORR kinetics. In addition, some investigators reported that the high ORR activity may be correlated to the formation of La-O and C-O bonds at the interfaces between carbon and La₂O₃ phase, which can promote electrons transfer between the ligands and lanthanum ions. As a result, some electrons will migrate to the unoccupied e_a orbitals splitted by La 5d orbitals of La₂O₃ through the electron transfer, which contributes to the oxygen adsorption that is the rate-determining step of ORR.^[17] Moreover, since La₂O₃ owns a moderate bandgap, which results in the ability to react with intermediate CO to form La2O3-CO bonds, and then the generated La₂O₃-CO bonds could react with oxygen containing species such as OH⁻ from water to form CO₂, which further relieves the poison of CO during catalysis.^[18-19]

Therefore, the electronic bandgap may be a key factor to govern catalytic activities toward ORR over La2O3 and other lanthanumbased compounds, because a suitable bandgap can not only promote the active oxygen adsorption but also desorb the adsorbed hydroxide into solution, and eventually lead to improved ORR catalytic activity. Furthermore, for lanthanumbased compounds like LaOHCO3 or La2O2CO3, their electronic bandgap can be tuned by their coordination environments composed of various oxygen-containing functional groups.^[20-22] Such variable bandgap would contribute to improve the catalytic activity by reducing the activation energy of catalyzing ORR over lanthanum-based compounds. In this way, La2O2CO3 or LaOHCO₃ should also exhibit good catalytic activity toward ORR, because they have similar electronic structures to La₂O₃ while the lanthanum ions in them are coordinated by different anions with different electron affinity, which results in varying bandgap. It has been verified that the reduced bandgap of some transition metal oxides plays an important role in determining the catalytic properties toward ORR.^[23] Unfortunately, La₂O₂CO₃ or LaOHCO₃ as electrocatalysts for ORR have received little attention by now, which needs further investigation.

In this work, we prepared three lanthanum compounds (La2O2CO3, La2O3, LaOHCO3) via a simple in-situ urea hydrolysis method, followed by annealing at different temperatures. And then, the energy level and bandgap of these samples have been determined by UV-vis and XPS measurements, and the obtained results show that La2O2CO3 owns the minimum bandgap with moderate energy level position among all these compounds. We also investigated the correlation between the bandgap and electro-catalytic activity of these compounds for ORR in alkaline solution. It is noted that the reduced bandgap of La₂O₂CO₃, derived by different oxygen functional groups, may be responsible for its improved ORR activity here. Understanding the origin of catalytic activity may be very important to develop cheap and stable lanthanum-based compound materials as next-generation electrocatalysts for ORR.

Results and Discussion

Characterization of lanthanum-based compounds

Figure 1(a) shows the schematic diagram of synthesis process for three lanthanum compounds, LaOHCO₃, La₂O₂CO₃, and La₂O₃. First, the added urea hydrolyzes into NH₃, CO₂ and OH⁻ at a given temperature of 85 °C. Then, the produced CO₂ and OH⁻ react with La³⁺ to form LaOHCO₃ on the carbon support. Finally, the lanthanum compound LaOHCO₃ decomposes into La₂O₂CO₃ at 550 °C and La₂O₃ at 800 °C under Ar atmosphere, respectively. Figure 1(b)-(d) show the morphologies of three asprepared lanthanum compounds. It can be observed that all these lanthanum compounds are mixed homogeneously with the carbon without obvious aggregation, as evidenced by the TEM images and BSE (Back Scattered Electron) images shown in Figure S1 and Figure S2 in the supporting information. The insets of Figure 1(b)-(d) show the particle sizes of the synthesized LaOHCO₃, La₂O₂CO₃, and La₂O₃, which is about 20, 18, 16 nm respectively. Moreover, Figure 1(e)-(g) show the parallel fringe of three lanthanum-based compounds, which

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corresponds to (121) plane of LaOHCO₃ orthorhombic phase, (130) plane of La₂O₂CO₃ monoclinic phase and (101) plane of La₂O₃ hexagonal phase, respectively. To further study the lattice structure of these compounds, XRD measurements were carried out and the obtained results are shown in Figure 1(h). The peaks located at 15.7°, 20.6°, 23.7°, 24°, 29.9°, 31.8°, 35.6°, 38.0°,43.3°,44.7° are attributed to the (011), (020), (111), (021), (121), (022), (200), (131), (221), and (212) planes of orthorhombic phase of LaOHCO3 [PDF card No.49-0981]. For La₂O₂CO₃, the recorded pattern peaks located at 13.0°, 25.5° 30.7°, 40.9°, 44.3°, 53.8° are (020), (120), (101), (141), (200), (231) planes of monoclinic phase of La2O2CO3 [PDF card No.48-1113], while peaks at 26.6°, 29.9°, 39.5°, 46.0°, 55.9° correspond to the (100), (101), (102), (110), (112), (201) planes of hexagonal phase of La2O3 [PDF card No.05-0602]. These outcomes further confirm the formation of three lanthanum compounds with different phases (orthorhombic LaOHCO₃, monoclinic $La_2O_2CO_3$ and hexagonal phase La_2O_3), via a simple in-situ urea hydrolysis method, followed by annealing at different temperatures shown in Figure 1(a).

The typical crystal structures of three lanthanum compounds are shown in Figure 1(i). The orthorhombic LaOHCO3 has a separated layer structure, where the CO₃²⁻ layer is parallel with (LaOH)²⁺ layer and oxygen atoms from CO₃²⁻ layer are located between the OH⁻ groups of two (LaOH)²⁺ layers.^[24] Similar with LaOHCO₃, the La₂O₂CO₃ also has a layer-like structure, while the carbonate is separated with the $(La_2O_2)^{2+}$ groups. However, because the hydroxyl of LaOHCO₃ is an electron donating group while carbonate is an electron withdrawing group, leading to the band strength of LaOHCO₃ should be stronger than La₂O₂CO₃. Such layer structure featured by LaOHCO3 or La2O2CO3 is different from that of La₂O₃ in which the LaO₂ species of La₂O₃ are directly stacked on each other.^[25] Compared with La₂O₃, the typical separated layer structure of La₂O₂CO₃ or LaOHCO₃ composed by (La₂O₂)²⁺/(LaOH)²⁺ and carbonate weakens the band strength, which may lead to special electronic structure.



Figure 1. (a) Schematic diagram of the synthesis process for three lanthanum compounds. (b)(c)(d) SEM and TEM (inset) images for LaOHCO₃, La₂O₂CO₃ and La₂O₃ on carbon. (e)(f)(g) HR-TEM images for these above lanthanum compounds nanoparticles. (h) XRD patterns for these above lanthanum compounds and (i) schematic diagram of LaOHCO₃, La₂O₂CO₃ and La₂O₃ crystal structure.

Electro-catalytic ORR activity of three lanthanum compounds

The electro-catalytic activity for ORR over each of the synthesized LaOHCO₃, La₂O₂CO₃, and La₂O₃ nanostructures was first investigated by cyclic voltammetry (CV) in N₂-saturated and O₂-saturated 0.1 M KOH solutions respectively, and the obtained results are shown in Figure 2(a). In the case of N₂-saturated CV curve, there is no redox feature observed and the value of current density is very small for these lanthanum-based compounds. However, for O₂-saturated CV curve, there is an apparent reduction peak with larger current and the onset potential of LaOHCO₃, La₂O₂CO₃, and La₂O₃ are 0.77, 0.81 and 0.79 V vs RHE, respectively. It indicates that the superior intrinsic ORR catalyzing performance of lanthanum compounds and La₂O₂CO₃ catalyst shows the best ORR activity compared with other lanthanum compounds.





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Figure 2. (a) CV curves for LaOHCO₃, La₂O₂CO₃ and La₂O₃ in 0.1 M KOH solution. The dashed line is tested in N₂-saturated solution and solid line is tested in O₂-saturated solution. The scan rates is 20 mV/s. (b) LSV curves corrected by the N₂-saturated solution results for these above lanthanum compounds in O₂-saturated 0.1 M KOH solution. The scanning rate is 5 mV/s. The current density is normalized by the work electrode area (0.247 cm²). (c) The value of j_K for three lanthanum compounds and the potential is 0.65 V vs RHE. (d) Specific mass activity for three lanthanum compounds and the potential is set as 0.65 V vs RHE. (e) Specific surface area activity. (f) The electron transfer number for three lanthanum compounds.

Moreover, the (RRDE) rotating ring-disk electrode measurements were carried out to further investigate the catalyzing ORR activities of these lanthanum-based compounds. As shown in Figure 2(b), all the lanthanum compounds exhibit highly ORR activity in alkaline solution, where La₂O₂CO₃ exhibits the most positive onset potential (0.8 V vs RHE) and the largest limited diffusion current density (~ 4 mA m⁻²) among all the tested samples. The slightly difference in limiting currents during ORR over these catalysts may be attributed to the different electrical conductivity for three lanthanum compounds. To further study the ORR kinetics over these catalysts, the kinetic current (I_K) values are obtained by the formula:

$1/I=1/I_L+1/I_K$

where I_K is the kinetic-limiting current, I is the current obtained at 0.65 V vs RHE, I_L is the limiting current. To obtain the kinetic current density (j_K), the corresponding measured current (I_k) was normalized by the surface area of each sample that is determined by Brunauer Emmett and Teller (BET) measurements shown in Figure S3. The obtained surface area of LaOHCO₃, La₂O₂CO₃ and La₂O₃ is 34.04, 61.53 and 47.69 m² g⁻¹ respectively. Therefore, the j_K results are shown in Figure 2(c). As is observed, the kinetic current density (j_K) of LaOHCO₃, La₂O₂CO₃, and La₂O₃ is 20.78, 54.97 and 25.43 μ A cm⁻², respectively, further indicating the highest catalytic activity of La₂O₂CO₃. Expect for the kinetic current density results, specific mass activities were also extracted for these catalysts to investigate their intrinsic catalytic activities and the results are

shown in Figure 2(d). At the typical voltage of 0.65 V vs RHE, the measured specific mass activity for LaOHCO₃, La₂O₂CO₃, and La₂O₃ is 7.07 A g⁻¹, 33.82 A g⁻¹ and 11.7 A g⁻¹, respectively. Figure 2(e) shows the specific surface area activities of three lanthanum compound catalysts at different potentials, which further confirms that the La₂O₂CO₃ has surprisingly high catalytic activity toward ORR, even under different potential conditions. As evidenced by Tafel plots in Figure S4, the ORR rate catalyzed by La₂O₂CO₃ is faster than that of La₂O₃ or LaOHCO₃. The over-potential of LaOHCO₃, La₂O₂CO₃ and La₂O₃ is determined by the difference value between the onset potential and oxygen reduction reaction potential (0.401 V).^[26] The derived over-potential of LaOHCO₃, La₂O₂CO₃ and La₂O₃ is 0.34, 0.337, 0.318 V, where La₂O₂CO₃ exhibits the minimum overpotential in three lanthanum compounds.

In addition, the Koutecky-Levich analysis were carried out to investigate the pathway of oxygen reduction, and the calculated average transfer electron number (n) is shown in Figure 2(f). As is seen, the average transfer electron number (n) of La₂O₂CO₃ is calculated to be 3.7 from 0.2 to 0.6 V vs RHE, and 3.2 for La₂O₃ and 3.0 for LaOHCO₃. The high electron transfer number for La₂O₂CO₃ demonstrates a nearly four-electron transferred process for oxygen reduction. However, the electrocatalytic activity of the lanthanum-based catalyst (La₂O₂CO₃) is slightly lower than that of Pt/C, as shown in Figure S5. It may be attributed to its poor electrical conductivity of the catalyst, compared with that of Pt/C. To improve conductivity of the catalyst, it is possible to further improve the activity.

Besides the catalytic activity, durability is another key parameter evaluating the performance of catalysts. Therefore, the stabilities for LaOHCO₃, La₂O₂CO₃, and La₂O₃ as well as Pt/C catalyst were measured via the chronoamperometric response method at 0.7 V (vs RHE) in 0.1 M KOH solution for 10000 s and the results are shown in Figure 3(a). As expected, all the lanthanum compounds exhibit better stability than Pt/C catalyst. Moreover, after 10000 s, there is still 93% current remaining for La2O2CO3, whereas only 90% for La₂O₃ and 88% for LaOHCO₃, indicating $La_2O_2CO_3$ is more stable than La_2O_3 or $LaOHCO_3$ during ORR process. The resistance for methanol poisoning is another important factor for the ORR catalysts. Accordingly, chronoamperometric measurements were performed at the potential of 0.7 V with a rotating rate of 900 rpm in 0.1 M O₂saturated KOH solution to investigate the methanol crossover effects for three lanthanum compounds as well as commercial Pt/C catalyst and the results are shown in Figure 3(b). For Pt/C catalyst, the injected methanol into O2-saturated KOH electrolyte at 1000 s leads to the ORR current sharply increase from cathodic current to anodic current because methanol oxidation alters oxygen reduction reaction,^[27] whereas the current density for three lanthanum compounds remains unaltered, indicating high immunity towards methanol and selectivity to ORR than Pt/C catalysts. The reason for such excellent durability and resistance to methanol poisoning is that the lanthanum compounds can react with methanol oxidation intermediate CO to form La-CO bonds, and then the generated La-CO bonds could react with the oxygen containing species such as OH⁻ from water to form CO₂, which further decay the poison of CO during catalysis.^[18-19] The good stability and high resistance to methanol poisoning should contribute the practical application of

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the very cheap $La_2O_2CO_3$ as next-generation catalyst for the ORR in alkaline solution, alternative to expensive Pt catalyst.



Figure 3. (a) Durability measurements for LaOHCO₃, La₂O₂CO₃, La₂O₃ and Pt/C for 10000 s, the potential is set as 0.7 V vs RHE. (b) Methanol crossover tests for LaOHCO₃, La₂O₂CO₃, La₂O₃ and Pt/C by injecting 1.5 ml methanol into the electrolyte (60 ml) at 1000 s. The chronoamperometric measurements were performed at the potential of 0.7 V vs RHE with a rotation rate of 900 rpm in 0.1 M O₂-saturated KOH solution.

Determination bandgap values of three lanthanum compounds

The bandgap values of LaOHCO₃, La₂O₂CO₃, and La₂O₃ were determined by UV-vis spectroscopy, and the results are shown in Figure 4. In Figure 4(a), the UV/vis spectroscopy absorbance spectra of the above lanthanum-based compounds show apparent band edge absorption under 250 nm. It is noted that the absorption coefficient of semiconductor has a characteristic relation:

$(\alpha hv)^n = B(hv - E_g)$

Where B is the semiconductor characteristic constant, n depends on the type of transition, which is 1/2 in this work. E_g is the bandgap that is the different value of conduction band and valence band, hv is photon energy and α refers to the absorption coefficient.^[28] Based on the deduced $(\alpha hv)^{1/2}$ - hv plots shown in Figure 4(a) inset, the calculated E_g values are shown in Figure 4(b). The obtained E_g value for LaOHCO₃, La₂O₂CO₃, and La₂O₃ is 3.88, 3.37 and 3.61 eV, respectively. However, the measured value of each compound is smaller than the derived value according to the first principles pseudo-potential calculation that is 4.51, 3.65, 3.8 eV for LaOHCO₃, La₂O₂CO₃, and La₂O₃ bulk materials, which should be ascribed to the quantum size effect for these lanthanum compound nanoparticles, leading decreasing value of E_g with decreasing particle size.^[20-21]

The different bandgap values for lanthanum-based compounds can be explained by their coordination environments, which mainly depends on the oxygen-containing functional groups and layer structures.^[25] As shown in Figure 1(i), among three lanthanum compounds, $La_2O_2CO_3$ has a separated layer structure that is composed by $(La_2O_2)^{2+}$ and carbonate, which weakens the band strength and leads to relatively small bandgap, as shown in Figure 4(b). La_2O_3 is composed by LaO_2 layers that are directly stacked on each other, which leads to the stronger band strength and larger bandgap of La_2O_3 than $La_2O_2CO_3$. For LaOHCO₃, its hydroxyl is an electron donating group that is easily to lose electron, while carbonate is an electron withdrawing group which is apt to obtain electron. As a result, LaOHCO₃ should have the largest E_q value.

The reduced band gap over lanthanum-based compounds would also contribute to improve the catalytic activity by reducing the activation energy of catalyzing ORR. This hypothesis has been

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verified by the results from Figure 4(c)-(d). Figure 4(c)-(d) has given the correlation of bandgap and electro-catalytic activities of three lanthanum compounds. As observed, with the decrease of bandgap value, the onset potential, j_K and specific mass activity are totally increased. La2O2CO3 with the minimum bandgap shows the maximum onset potential, kinetic current density (i_K) and specific mass activity shown in Figure 4(d), further illustrating the bandgap may be a key factor to control the ORR activity over these lanthanum compounds. On the one hand, the decreased bandgap will lead to an increase of electrical conductivity of lanthanum compounds, which is very important to improve the nonconductive oxide catalytic activity. On the other hand, the decreased bandgap can promote the oxygen reduction kinetics by facilitating oxygen absorption and electron transfer from catalyst bulk to the surface adsorbing oxygen species, which can reduce the activation energy of catalyzing ORR. This conclusion has been proved by transition metal oxide like Co₃O₄ as catalysts for the ORR.^[29]



Figure 4. (a) Absorption spectra for LaOHCO₃, La₂O₂CO₃ and La₂O₃ nanoparticles by UV-vis and the inset is apparent energy gap of LaOHCO₃, La₂O₂CO₃, La₂O₃ nanoparticles. (b) The calculated bandgap for LaOHCO₃, La₂O₂CO₃, La₂O₃ nanoparticles. (c) Relationship between onset potential and bandgap and (d) relationship between the j_K, specific mass activity and bandgap for three lanthanum compounds.

The origin of catalytic activity for lanthanum compounds.

We investigate the origin of ORR catalytic activity for lanthanumbased compounds based on their intrinsic electronic bandgaps. XPS measurements were employed to locate the valance band level, and the results are shown in Figure 5(a). Their valance band maximum (VBM) positions are determined by the leading edges linear extrapolation of valance band (VB) spectra to the base line. As is shown, the calculated VBM for LaOHCO₃, La₂O₂CO₃, and La₂O₃ is 1.89, 1.66, -0.45 eV respectively, which corresponds to the potential (vs NHE) is 1.48, 1.26, -0.85 V.^[30] Therefore, the value of conduction band (CB) for LaOHCO₃, $La_2O_2CO_3,\ and\ La_2O_3$ is -2.39, -4.46, -2.11 V vs NHE, respectively. The energy level diagram for three lanthanum compounds is shown in Figure 5(b). According to the diagram, both the VB and CB levels of La_2O_3 are more negative than the reduction potential of O₂/OH⁻ (0.401 V), which makes it difficult for the electrons under excitation to participate in the electrochemical reaction of oxygen reduction. Different from La₂O₃, La₂O₂CO₃ and LaOHCO₃ have a more positive VB level, and the reduction potential of O_2/OH^- (0.401 V) is between the VB and CB of La₂O₂CO₃ and LaOHCO₃, which contributes the covalent electrons under excitation from VB to CB to participate the oxygen reduction. Moreover, compared with LaOHCO₃, La₂O₂CO₃ has a more negative VB level and more positive CB level, indicating that covalent electrons in VB level owns higher energy to transfer into CB level under excitation, and then easily transfer from CB to adsorbed oxygen molecules. As a result, based on the energy level structure, La₂O₂CO₃ with the smallest bandgap and moderate energy level structure of VB and CB should have the highest ORR activity among all the compounds. Figure 5(c) shows the electron transfer process in the catalyzing ORR of La₂O₂CO₃. During the ORR over La₂O₂CO₃, covalent electron of La2O2CO3 is first excited from VB level under the condition of impressed current, then the excited electron transfers from VB into CB due to the moderate bandgap value. The excited electron has sufficient potential to transfer into the unoccupied π^*_{2p} orbitals of oxygen, leading to a strengthen oxygen adsorption, which promotes the reduction of oxygen.[31-33 The high ORR activity of La₂O₂CO₃ has been verified by the results from Figure 2. The detailed ORR process over La₂O₂CO₃ has been shown in Figure 5(d). For lanthanum-based compounds, their bandgaps and energy level structure of VB and CB can impact the ORR activity of them together. This conclusion can be confirmed by incomplete linear relationship of the activity and bandgap as an activity description, as shown in



Figure 5. (a) Valence band maximum for LaOHCO₃, La₂O₂CO₃ and La₂O₃ nanoparticles determined by XPS valance band spectra via linear extrapolation of the leading edges and the base lines. (b) Energy level diagram for the LaOHCO₃, La₂O₂CO₃ and La₂O₃ compounds. (c) and (d) Schematic diagram for electron transfer process of La₂O₂CO₃ in the ORR electro-catalytic process.

Concerning that the energy level of lanthanum-based compounds plays an important role in catalyzing ORR, we also study the influence of $La_2O_2CO_3$ energy level on the ORR pathway apart from the bandgap. Figure 6(a) gives the possible schematic diagram of electron transfer process of $La_2O_2CO_3$ during ORR, based on the energy level of both VB and CB, relative to the redox potentials of O_2/HO_2^- and O_2/OH^- pairs as references. We can observe that the reduction potential of

 O_2/HO_2^- or O_2/OH^- is in the middle position between the VB and CB levels. As a result, the excited electron occupied in CB originated from VB of La₂O₂CO₃ can transfer into the O₂/HO₂ level to generate HO₂ through a 2-electron pathway; at the same time, these excited electrons can also transfer into the O₂/OH⁻ level to produce OH⁻ via a 4-electron pathway during, as shown in Figure 6(a). Since the reduction potential of O_2/HO_2 pair is more negative than O₂/OH⁻ pair, it is possible that many transferred electrons will occupy the O₂/HO₂⁻ level, which results in a lot of H₂O₂ produced as ORR intermediate product. However, as shown in Figure 6(b), the H_2O_2 production (26%) on the $La_2O_2CO_3$ catalyst is much lower than the OH⁻ (74%), as shown in Figure 6(c). The high OH⁻ production over this catalyst can be explained by two aspects as following. On the one hand, for the La₂O₂CO₃/C hybrid catalyst, there remains a strong chemical interaction between La₂O₂CO₃ and carbon support in their hybrid, which can facilitate the ORR undergoing through the 4-electron pathway to generate dominated OH rather than H₂O₂, as confirmed by recently published report.^[13] This leads to the low production of H_2O_2 with respect to OH^- produced by the catalyst, although the energy level diagram in Figure 6(a) is beneficial to the formation of H_2O_2 . On the other hand, considering that the lanthanum compound has an ability to chemical disproportionation for hydrogen peroxide (HO₂⁻), which can lead to that the HO2⁻ species produced at the energy level of O₂/HO₂⁻ level undergo prompt chemical disproportionation into O_2 and OH^- species.^[34-35] The generated O_2 in this stage adsorbs on the catalyst surface, which can be utilized for further oxygen reduction once again. Moreover, it has been reported that existence of (CO32-) in La2O2CO3 leads to a larger radius, which are not only beneficial for isolating the active sites but also for store oxygen.^[36] Thus, the ability of oxygen storage can facilitate the reuse of O₂ from hydrogen peroxide decomposition process, leading to an enhanced ORR activity. The above two aspects should be responsible for the low hydro-peroxide yield on this catalyst shown in Figure 6(c) and the highly ORR activity (Figure 2(a) and (b)). Therefore, we conclude that the ORR process catalyzed by lanthanum-based compound via a nearly 4-electron pathway (apparent 4-electron mechanism). This conclusion is in agreement with the results shown in Figure 2(f).



Figure 6. (a) Schematic diagram for HO₂ production in the ORR process. (b) RRDE plots of $La_2O_2CO_3$ in 0.1 M KOH solution with the rotating rate at 1600 rpm. (c) HO₂ ratio and OH ratio of $La_2O_2CO_3$ at the potential of 0.7 V vs RHE.

Conclusions

Three lanthanum compounds (LaOHCO₃, La₂O₂CO₃, and La₂O₃) were synthesized via an in-situ urea hydrolysis method, followed by annealing at different temperatures. The obtained LaOHCO₃

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and La₂O₂CO₃ own layer structure while La₂O₃ has a directed stack layer structure. The particle sizes of the synthesized LaOHCO₃, La₂O₂CO₃, and La₂O₃ are about 20, 18, 16 nm respectively. Compared with the other two compounds, the La₂O₂CO₃ exhibits the best electro-catalytic activity, the lowest H₂O₂ production and superior durability for the ORR in 0.1 M KOH solution. The improved ORR activity of the lanthanum compound can be attributed to its minimum bandgap and moderate value of conduction band (CB) and valance band (VB) in electronic structure, which facilitates the excited electrons transferring into O2/HO2 or O2/OH levels to produce HO2 or OH species via a 2/4-electron pathway during the ORR process. Considering that the lanthanum compound has the ability of chemical disproportionation for hydrogen peroxide (HO2), it can lead to HO₂ species undergoing a prompt chemical disproportionation into O₂ and OH⁻ species. The generated O₂ in this stage adsorbs on the La2O2CO3 surface that is beneficial for oxygen storage due to its unique layered structure. It can facilitate the reuse of O₂ from hydrogen peroxide decomposition process, which further contributes the ORR kinetics. Therefore, understanding the origin of the catalytic activity may be very important to develop cheap and stable lanthanum-based compound materials as next-generation electrocatalysts for the ORR.

Experimental Section

Synthesis of materials

Prior to the preparation of preferred La2O2CO3 and La2O3, LaOHCO3 was initially prepared via a simple in-situ urea hydrolysis method. The typical preparing procedure of LaOHCO3 is shown as follows. First, 70.1 mg of La(NO₃)₃•6H₂O and 780 mg urea were dissolved in 65 ml deionized water (18.2 M Ω) to form a clear solution. After that, 100 mg carbon black (Vulcan XC-72, Cabot) was added into the solution as disperser to control lanthanum compounds particle size and increase the electronic conductivity of lanthanum-based catalyst. The mixed solution was then heated at 85 °C for 2 h with vigorous stirring and the resulting mixture was washed with deionized water and ethanol for several times and then dried for five hours at 80 °C, which obtained the LaOHCO3 sample. Then, the as-synthesized LaOHCO3 were used as precursor to prepare $La_2O_2CO_3$ and La_2O_3 samples by calcining at 550 $^\circ C$ and 800 $^\circ C$ for 2 h under Ar atmosphere, respectively. The mass ratio of these lanthanum compounds to their carbon supports is fixed at 10:1 by varying the added amount of carbon black, as shown in Figure S6.

Characterization of materials

The morphologies of these lanthanum compounds were observed via the transmission electron microscopy (TEM) (JEOL TEM 2010 microscope) and scanning electron microscopy (SEM) (FE-SEM, JEOL, JSM-6701F), respectively. The crystal structure of each lanthanum compound was determined by X-ray diffraction patterns (XRD) from Rigaku RINT 2200 V/PC at 30 kV and 40 mA, where the scan rate was 4 °/min from 10° to 60°, and the schematic diagram for lanthanum compounds crystal structure was drawn by Diamond 3.1. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was applied for the valence band spectra of three lanthanum compounds and the XPS spectra were calibrated by C 1s at 285.0 eV. UV/vis spectroscopy on a UV2450 was used to characterize the optical absorbance of the pure LaOHCO₃, La₂O₂CO₃, and La2O3 nanoparticles which were dissolved in deionized water, and the slit width was set at 2.0. The surface area of lanthanum compounds was measured by BET (Quadrasorb SI-MP). The amount of lanthanum compound relative to carbon support was determined by thermo-

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gravimetric and differential thermo-gravimetric analysis (TG-DTA, Thermoplus TG8120, Rigaku)

Electrochemical measurement of materials

All the electrochemical measurements for these lanthanum compounds (LaOHCO₃, La₂O₂CO₃, and La₂O₃) were conducted by a rotating ringdisk device (AFCBP1 type, PINE, USA) (RRDE) in 0.1 M KOH solution, where the saturated calomel electrode (SCE) was acted as a reference electrode and the platinum wire was a counter electrode. For preparing hybrid catalysts, 5 mg catalyst was mixed with 1 ml ethanol and 50 µl Nafion (5 wt%), and then 25 μl of the ink was dropped at the working electrode (0.247 cm²). The cyclic voltammetry (CV), rotating ring-disk electrode (RRDE) experiments and chronoamperometry response were contained in our study. The scanning rate of the CV testing was performed at 20 mV s⁻¹ and the potential range was from 0 V-1.1 V vs RHE. The RRDE experiment was tested at 5 mV s⁻¹ with the rotating rates changing from 400 rpm to 1600 rpm. The ring potential of RRDE measurement was fixed at 0.50 V (vs RHE). As for the durability experiment, all the lanthanum compound catalysts were tested at the same potential of 0.7 V vs RHE.

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Keywords: lanthanum compounds• oxygen reduction reaction • bandgap• hydro-peroxide decomposition • electronic energy level

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