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Oxygen-deficient BaTiO$_{3-x}$ perovskite as an efficient bifunctional oxygen electrocatalyst

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Abstract

Perovskite oxide catalysts have emerged as the most promising bifunctional oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalysts for electrochemical energy conversion and storage. In this work, a new type of oxygen-deficient BaTiO$_{3-x}$ has been synthesized using a sol-gel method followed by a reductive heat treatment at 1300 °C in vacuum. The prepared perovskite nanoparticles have an average particle size on the order of 100 nm with uniform size distribution. X-ray diffraction shows that this perovskite catalyst consists of a significant amount of hexagonal BaTiO$_{3-x}$. State-of-the-art IrO$_2$ nanoparticles were also prepared in this work, which were used for reference and have excellent OER activity. Importantly, the oxygen-deficient perovskite catalysts exhibited high catalytic activity simultaneously for the ORR and the OER in alkaline electrolyte. The more challenged OER activity measured with the perovskite exceeds the IrO$_2$ catalyst at relatively low potentials (<1.6 V) evidenced by a much reduced onset potential (1.32 V) and increased current density. In order to clearly elucidate the structure of the oxygen-deficient BaTiO$_{3-x}$ catalysts, X-ray and neutron diffraction experiments were further carried out, indicating that the hexagonal phase in the best performing BaTiO$_{3-x}$ catalyst is oxygen-deficient with a stoichiometry of BaTiO$_{2.76}$. The oxygen vacancies in the perovskite crystal structure may lead to vastly enhanced electrocatalytic activity toward the ORR and OER. This work demonstrates a new type of highly efficient perovskite bifunctional catalyst for electrochemical energy technologies relying on oxygen electrocatalysis.

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Introduction

Development of cost-effective and highly active catalysts for electrochemical energy storage and conversion applications is a critical element in currently studied sustainable energy technologies. In particular, metal-air batteries represent the most promising energy storage systems for portable electronics, electrical vehicles, and stationary applications for storing the clean energy obtained from wind, solar, and power plants. Unlike the traditional intercalation electrodes in Li-ion batteries, the porous air cathode in the metal-air cell is capable of taking reactant \( \text{O}_2 \) from the atmosphere, instead of storing it in the electrodes. The unique configuration results in a vastly improved theoretical specific energy density of 1086 W h kg\(^{-1}\) for Zn-air and 5028 W h kg\(^{-1}\) for Li-air cells, two of the most promising metal-air batteries [1]. These advanced electrochemical energy technologies; however, rely greatly on the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which are a pair of the most important and technologically pertinent electrochemical reactions [1-3]. However, the ORR and OER typically have very high overpotentials with slow kinetics, requiring catalysts containing large amount of precious metals such as Pt and Ir [2]. These precious metals are prohibitively expensive and their supply is limited, which make these catalysts unsustainable for modern society [4].

To avoid the use of precious metal catalysts, some promising nonprecious metal catalysts (NPMCs) have been studied in the past decade [5-10]. They include organometallic components, nonprecious-metal chalcogenides, and nitrogen-doped carbon catalysts [1,11-16]. Among them, nitrogen-doped carbon composite catalysts possess high activity and stability for the ORR, especially in alkaline media exceeding the state of the art Pt catalysts [1,17]. Despite this significant progress developing precious metal-free catalysts, their activity and durability for the OER remain significantly insufficient [18-23]. As a matter of fact, compared to the ORR, electrocatalysis of OER is more challenging due to the extremely oxidative conditions at high potentials (>1.4 V vs RHE), where most of currently studied carbon-based catalysts degrade due to the rapid oxidation of carbon [24-26]. Iridium oxide (IrO\(_2\)) is the most active and stable catalyst reported to date for the OER [19]. Unfortunately, the high cost and earth-limited supply of this precious metal represents a major challenge for widespread application of these reversible electrochemical clean energy technologies [1,2,5,11,27].

During the exploration of NPMCs to replace the expensive IrO\(_2\) catalysts, several cost-effective perovskite oxides have been identified as promising OER catalysts showing high activity [7,19,28-33]. Meanwhile, significant progress has also been made in order to acquire understanding of the mechanism and parameters that govern the ORR and OER activities of perovskite oxide catalysts [7,29,30,32,34]. Perovskites usually have an \( \text{ABO}_3 \) formula, where \( \text{A} \) is most often a rare-earth or alkaline-earth metal and tends to be a larger and more electronegative metal, while \( \text{B} \) is a transition metal which is relatively smaller and more electronegative. The ideal unit cell of a perovskite has oxygen ions in the face centered cubic positions, the \( \text{A} \) cations in the corner cube position, and the \( \text{B} \) cations in the body center cubic position. This results in the \( \text{A} \) cation being surrounded by a cuboctahedron of 12 oxygen ions and the \( \text{B} \) cation being surrounded by 6 oxygen ions in an octahedron [35-37]. The ORR and OER mechanisms on the perovskite are also analyzed, indicating both the ORR and OER can proceed via four-electron transfer steps. The rate-determining steps (RDS) are the O-O bond formation and the proton extraction of the oxy-hydroxide group [7,19]. Previous studies have concentrated on the substitution of the \( \text{A} \) or \( \text{B} \) sites for the improved catalytic properties. Such substitution would provide a convenient activity descriptor for the first-row transition metal oxides such as NiCo\(_2\)O\(_4\), LaNiO\(_3\), and Ba\(_{1-x}\)Sr\(_x\)Fe\(_{1-y}\)Co\(_y\)O\(_3\) [34,38]. However, all of these studied perovskite catalysts are still far from sufficient when compared to the IrO\(_2\) catalysts.

In this work, we studied a novel oxygen-deficient BaTiO\(_3\)\(_{1-x}\) for the first time, as an efficient catalyst for the ORR and OER. The oxygen deficient BaTiO\(_3\)\(_{1-x}\) nanoparticles were synthesized from a sol-gel method. The motivation of this work is to intentionally create a large number of oxygen defects, especially for regions near the surface. These oxygen vacancies can behave as donors or acceptors, leading to semiconducting behavior over a thin surface layer. There is some evidence that these vacancies act as a source of additional electrons beyond the surface screening charges that can be emitted during electrical chemical catalytic reactions. Herein, the oxygen-deficient BaTiO\(_3\)\(_{1-x}\) (BaTiO\(_x\)) determined by the time-of-flight neutron powder diffraction exhibits enhanced ORR and excellent OER activities comparable to the state-of-the-art IrO\(_2\) nanoparticles. It holds great promise as an efficient bifunctional cathode catalyst for reversible electrochemical energy storage and conversion in metal-air batteries and fuel cells. These findings may represent a new paradigm of NPMC system for bifunctional oxygen reaction catalysts.

Experimental section

Sol-gel BaTiO\(_3\) synthesis

Barium acetate, titanium isopropoxide, acetic acid, 2-methoxy ethanol, and ammonium hydroxide (NH\(_4\)OH) were purchased from Sigma Aldrich Chemical Corporation (St. Louis, MO, USA). BaTiO\(_3\) (BTO) nanoparticles were synthesized using barium acetate (reagent grade) and titanium(V) isopropoxide (purity > 98%) [39]. During the synthesis, acetic acid was used as the solvent to dissolve barium acetates; 2-methoxy ethanol (> 99%) was used to stabilize titanium(V) isopropoxide. Typically, stoichiometric proportions of barium acetate (1.0 mol of Ba) powders were dissolved in 200 mL of acetic acid by continuous magnetic stirring at 200 rpm for 1 h. Meanwhile, 2-methoxy ethanol (100 mL) was added to the titanium(V) isopropoxide (1.0 mol of Ti) by continuous magnetic stirring at 200 rpm for 1 h to form a separate solution at room temperature. Then the Ba solution was added drop wise to the as-prepared Ti solution with the assistance of a burette. The pH of the solution was controlled in a range of 6.8-7.2 by using 5.0 M NH\(_4\)OH solution. Subsequent refluxing resulted in the formation of a thick white colored gel. De-ionized water (200 mL) was added to it, and the solution was stirred magnetically at 300 rpm for 4 h. This suspension was then vacuum filtered followed by an overnight drying at 90 °C. These drying procedures resulted in the formation of whitish BaTiO\(_3\) cakes, which were then ground to powders using a high purity Al\(_2\)O\(_3\) mortar and pestle followed by screening with a 325 mesh sieve. The “screened sol-gel” powders were calcined at three different conditions, i.e. air, argon and vacuum as described in details below.
Some of the resulting powder was loaded into a high purity Al₂O₃ crucible and calcined at 950 °C in air for 2 h in an air furnace (MRIX, Cincinnati, OH) to form stoichiometric BaTiO₃. This 950 °C air calcined powder will be designated as “BTO-950AIR”. Some of the “screened sol-gel” powder was loaded into a graphite crucible and heat treated at 1300 °C in argon for 2 h in a graphite resistance furnace (Thermal Technology, Santa Rosa, CA) to investigate the effect of reducing atmosphere. Both the heating rate and cooling rate were maintained at 400 °C h⁻¹. This 1300 °C-argon treated powder will be designated as “BTO-1300AR”. Some of the “screened sol-gel” powder was loaded into a graphite crucible and heat treated at 1300 °C under vacuum for 2 h in a graphite resistance furnace to investigate the effect of extreme reducing atmosphere. This 1300 °C-vacuum treated powder will be designated as BTO-1300VAC.

Then, 25 g of BTO-950AIR, BTO-1300AR, and BTO-1300VAC powders were mixed with 10 wt% of carbon black (2.5 g) (Vulcan XC72, CABOT, Billerica, MA, USA), respectively. The addition of carbon black is to enhance electrical conductivity of the oxide catalysts. Typically, the BTO-950AIR, BTO-1300AR and BTO-1300VAC powder was mixed with carbon blacks and loaded into three 500 ml high density polyethylene (PE) bottles, respectively, with half full of 13 mm high purity zirconia grinding media. De-ionized water (100 g) was then weighed into all three PE containers with a total solid loading of about 30%. The ball-milling process was carried out on a roller at a rotating speed of 100 rpm for about 2 h. After ball milling, the slurries were poured into three different glass beakers and dried overnight in an oven at 90 °C. All three dried cakes were ground using a high purity Al₂O₃ mortar and pestle, which were then screened by a 325 mesh stainless steel sieve.

**Synthesis of IrO₂**

In order to directly compare the prepared perovskite to state-of-the-art IrO₂ catalysts in terms the OER activity, we also prepared IrO₂ nanoparticles in this work. Iridium chloride hydrate (IrCl₃·xH₂O) (99.98%) powders were purchased from Aldrich Chemical, St. Louis, MO, USA. A sol-gel synthesis was used to prepare nanoparticle IrO₂. Typically, 5.0 g IrCl₃·xH₂O was added to 20 ml of acetic acid at continuous magnetic stirring for about 1 h. When 100 ml of 5.0 M ammonium hydroxide (NH₄OH) was added to the IrCl₃ solution in drops, the solution turns to a black color gel. The solution was continuously stirred at 300 rpm for about 4 h with a pH in the range of 6.8 to 7.2. This gel was then dried in 90 °C in air overnight. The resulting black cakes were then ground to powders that were further screened through a 325 mesh stainless steel sieve. The screened sol-gel powders were loaded into a high purity Al₂O₃ crucible and calcined at 550 °C for 2 h under a constant flow of pure oxygen with a flow rate of 10 ml min⁻¹ in a tube furnace (Delta H Technologies, Carroll, OH, USA). This resulting sample was designated as “Ir-550”.

**Physical characterization**

Scanning electron microscopy (SEM) was used to determine the particle size and morphology of synthesized samples. Transmission electron microscope (TEM) thin foils were prepared by touching Cu grids having an ultrathin carbon substrate supported on lacy carbon to the dry powder and tapping off excess material. TEM was performed on an FEI (Hillsboro, Oregon, USA) Titan 80-300 operating at 300 kV with the image corrector tuned to approximately 1 Å resolution. High-resolution images were obtained and processed using Gatan’s Digital Micrograph software, which has a standard fast Fourier transformation (FFT) function for crystallographic analysis. Selected area diffraction (SAD) patterns were collected using standard techniques and were processed using the PASAD set of plug-ins for Digital Micrograph. Powder X-ray diffraction (XRD) patterns were recorded for all samples in the 2θ range of 10 to 90° on a Bruker D8 Advance X-ray diffractometer (Bruker-AXS, Inc., Madison, WI) using CuKα radiation (λ=0.1542 nm) at 40 kV and 40 mA with Soller slits and a diffracted beam graphite monochromator. Time-of-flight neutron powder diffraction (NPD) data were collected on the BTO-1300VAC nanoparticles with 10 wt% carbon using the HIPD instrument at the Lujan Neutron Scattering Center at Los Alamos National Laboratory. HIPD has 8 detector banks located at ±153°, ±90°, ±40°, ±14° and covers a d-spacing range of 0.4-38.0 Å. Approximately 4 g of sample was loaded into a vanadium can and measured for 16 h at 300 K. The diffraction data were analyzed by Rietveld refinement using the General Structure Analysis System (GSAS) software.

**Electrochemical measurements**

Electrochemical characterization of the catalysts was carried out using a rotating disk electrode (RDE) with a 5.0 mm-diameter glassy carbon. All RDE measurements were performed using CHI Electrochemical Station (Model 760e) in a conventional three-electrode cell with 0.1 M NaOH electrolyte at room temperature. An Ag/AgCl electrode in 3.0 M NaCl (0.229 V vs SHE) was used as the reference electrode. The reference potentials vs reversible hydrogen electrode (RHE) used in this work were calibrated using a Pt wire coated with electrodeposited Pt black electrode by bubbling H₂ in 0.1 M NaOH electrolyte. To avoid any potential contamination of the nonprecious metal catalyst by platinum, all RDE experiments were carried out using a graphite rod as the counter electrode. Catalyst loading for all BaTiO₃ and IrO₂ samples was controlled at 0.6 and 0.06 mg cm⁻², respectively. As for the OER and ORR tests, steady-state polarization plots were recorded in a potential range from 0.2 V to 1.9 V using staircase voltammetry with a potential step of 30 mV holding for 30 s. The electrolytes were saturated with O₂ and N₂ for the ORR and OER tests, respectively. The disk rotation rates for the ORR ranged from 400 to 2500 rpm.

**Results and discussion**

**BaTiO₃ – x catalyst synthesis and morphology**

Figure 1(a) is an SEM micrograph showing the typical air calcined nanoparticles of BTO-950AIR, showing severe agglomeration due to the bonding reaction in air at 950 °C. The particle size distribution ranges from 120 to 260 nm with an average particle size of about 190 nm. Figure 1(b) demonstrated the typical particle size and morphology of the “BTO-1300AR” sample. The particle sizes were smaller and...
found to range from 90 to 150 nm with an average size around 120 nm, showing less significant agglomeration of these nanoparticles due to the use of argon atmosphere. Meanwhile, as shown in Figure 1(c), the typical particle size of the “BTO-1300VAC” nanoparticle ranges from 90 to 130 nm, and the average particle size is on the order of 100 nm. Thus, compared to the BTO-1300AR sample (Figure 1b), the particle size of BTO-1300VAC is about the same, however very little agglomeration occurred in these BTO-1300VAC particles. It is believed that the formation of organic or inorganic volatiles such as CH₄, CH₃OH, CO, or CO₂ resulting from the decomposition of the acetate during the vacuum calcination helps disperse the nanoparticles uniformly and minimizes the possible agglomeration during high-temperature treatments. Although both BTO-1300AR and BTO-1300VAC powders were calcined at a much higher temperature (i.e. 1300 °C) compared to BTO-950AIR (i.e., 950 °C), which usually leads to particle growth, the inert environment is able to slow down oxygen diffusion during the calcination process. The mitigated oxygen diffusion further decreases the reaction bonding among the nanoparticles at high temperatures, resulting in less agglomerated morphologies compared to the BTO-950AIR nanoparticles.

**Structure analysis of oxygen-deficient BaTiO₃₋ₓ**

Rietveld refinement of the XRD pattern of the BTO-950AIR sample (Figure 2) shows that the air calcined nanoparticles are single phase tetragonal BaTiO₃ (t-BaTiO₃). No impurity phases were present. For the nanoparticles calcined in an Ar atmosphere, although the major phase of BTO-1300AR nanoparticle is tetragonal BaTiO₃, the XRD pattern also indicates that there has been a reaction between the BaTiO₃ and the hydrocarbon to form some TiC and BaCO₃. Refinement of the phase fractions gives 65% t-BaTiO₃, 13% TiC, and 22% BaCO₃ by weight percent.

In contrast, the XRD pattern of the BTO-1300VAC sample is quite different from those of BTO-950AIR and BTO-1300AR. It shows a mixture of both tetragonal and hexagonal BaTiO₃ (h-BaTiO₃). This sample also appears to have reacted with the hydrocarbon but to a much lesser extent. Refinement of the phase fractions gave 63% t-BaTiO₃, 29% h-BaTiO₃, 5% TiC, and 3% BaCO₃ by weight percent. Thus, BTO-1300VAC shows a significant structural difference when compared to BTO-950AIR and BTO-1300AR. There is significant presence of h-BaTiO₃ in the BTO-1300VAC sample. The BTO-950AIR nanoparticles contain a single phase of t-BaTiO₃, which indicates that the stoichiometric t-BaTiO₃ does not have electrochemical catalytic activity for the ORR and OER even though they are on the nanoparticle scale. Similar to t-BaTiO₃, both TiC and BaCO₃ are not electrochemically active too.

The crystal structures of the tetragonal and hexagonal forms of BaTiO₃ are shown in Figure 3. The tetragonal form consists of a three dimensional infinite network of corner sharing TiO₆ octahedra with the Ba atoms in the cubooctahedral cavities. In this structure, the Ti⁴⁺ cations undergo polar off-center distortions towards a corner of their octahedron. In the hexagonal structure, the TiO₆ octahedra share both corners and faces, giving rise to a more complex structure.

In order to further elucidate the possible active species associated with the h-BaTiO₃, neutron powder diffraction was carried out for the BTO-1300VAC sample (Figure 4). The data were further refined in order to gain more structural information on the oxygen content of the BaTiO₃ phases in this sample, as neutrons have a much greater sensitivity to oxygen atoms than X-rays do. In the Rietveld method, it is possible to directly refine to oxygen atom site occupancies in the structural model as free variables in the refinement. For the tetragonal BaTiO₃, the oxygen site occupancies

![Figure 1](https://www.example.com/figure1.png)

**Figure 1** SEM images for (a) typical BTO-950AIR (950 °C in air), (b) BTO-1300AR (1300 °C in argon), and (c) BTO-1300VAC (1300 °C in vacuum) samples.

![Figure 2](https://www.example.com/figure2.png)

**Figure 2** XRD patterns for BTO-950AIR, BTO-1300AR, and BTO-1300VAC nanoparticles. The air calcined BTO-950AIR nanoparticle has a single phase of tetragonal t-BaTiO₃. The major phases of BTO-1300AR nanoparticle are tetragonal BaTiO₃, TiC, and BaCO₃. BTO-1300VAC shows a mixture of both tetragonal as well as hexagonal h-BaTiO₃ in addition to some TiC and BaCO₃.
refined to a value of 1.01(1), indicating that there are no vacancies in this phase. Oppositely, the oxygen site occupancies in the hexagonal phase refined to be 0.92(3), which corresponds to BaTiO$_2$.76, and shows that the hexagonal phase is the oxygen deficient one. As the hexagonal phase is not the only phase in the neutron powder diffraction pattern, it was not possible to determine if Ba vacancies or formation of Ti$^{3+}$ is the major charge compensation mechanism. A possible mechanism was proposed to explain the formation of oxygen-deficiency during the high-temperature in vacuum. Due to the low O$_2$ partial pressure, BaTiO$_3$ nanoparticles tend to lose oxygen during high temperature treatments. Furthermore, the high oxygen concentration gradient at high temperature results in a strong diffusion of the oxygen atoms to the surface of the BaTiO$_3$ nanoparticles and the high surface area of the nanoparticles further enhances the oxygen diffusion from the surface to the outside low partial pressure atmosphere.

In the BTO-1300VAC sample, oxygen deficiency was clearly verified. However, the perovskite structure nearly never has B-site (Ti$^{4+}$) deficiency as this is extremely energetically unfavorable. Ba$^{+2}$ deficiency is certainly possible and the Ba to Ti ratio is less than 1. However, this would be consistent with oxygen deficiency since Ba deficiency is one of the most likely charge compensation mechanisms to counter the loss of oxygen. BaTiO$_3$ is normally tetragonal under ambient conditions, with the hexagonal phase being the high temperature form of BaTiO$_3$. However, other studies have shown that creating significant concentrations of oxygen vacancies can further stabilize the hexagonal form[40–43], which is consistent with our results. The oxygen deficient $h$-BaTiO$_{3-x}$ creates a large number of oxygen defects, especially for regions near the surface. These oxygen vacancies can behave as donors or acceptors, leading to semiconducting behavior over a thin surface layer. These vacancies might act as a source of additional electrons beyond the surface screening charges that can be emitted during electrical chemical catalytic reactions. Generally, it might be possible to create an oxygen deficient $t$-BaTiO$_{3-x}$ when the x is very small and the tetragonal structure can be maintained. However, when the oxygen deficiency reaches to a high level, the structure becomes hexagonal to reach the lowest energy and maintain the stability of the structure.

**IrO$_2$ reference catalyst synthesis and morphology**

A homemade IrO$_2$ catalyst was also prepared as a reference for comparison in this work. Figure 5a is the XRD pattern of the Ir-350 powders after oxidation during a heat treatment in pure oxygen at 550 °C for 2 h. The broad peaks of the XRD pattern indicate that most of the particles are at the nanoscale. The average particle size was estimated from the full-width-at-half-maximum peak widths using the
Scherrer equation to be about 10 nm. The XRD pattern also indicates that the Ir-550 powder contains about 93% IrO₂ nanoparticles and about 7% Ir nanoparticles. It is believed that the reason for the small fraction (7%) of Ir nanoparticles is due to incomplete oxidation. IrO₂ is well known for its high oxidation resistance by forming an oxide protecting layer. Thus, oxygen cannot penetrate through the whole IrO₂ layer, thereby leaving a small fraction of un-oxidized Ir metal inside these particles. A similar synthesis of IrO₂ nanoparticles was also developed by Lee et al.

Figure 5 (a) XRD pattern of the Ir-550 powder after oxidation via a heat treatment in pure oxygen at 550 °C for 2 h and (b) HR-TEM images to determine nanoparticle size ranging from 3 to 20 nm with an average particle size of about 11 nm. The lower left insert is a Selected Area Diffraction (SAD) pattern from IrO₂ nanoparticles, and the lower right insert is a Fast Fourier Transform (FFT) from the high-resolution TEM image. Both SAD and FFT can be indexed as consistent with body centered tetragonal IrO₂.

Figure 6a compares the ORR and OER activity for the BTO-950AIR, BTO-1300AR, BTO-1300VAC, and the Ir-550 samples prepared in this work. As Ir and IrO₂ are electron conductors, Ir-550 catalyst did not have carbon addition, while BTO-950AIR, BTO-1300AR and BTO-1300VAC contain about 10 wt% of free carbon. In 0.1 M NaOH, our homemade IrO₂ catalyst (Ir-550 sample) demonstrated an onset potential at 1.50 V for the OER. This result is close to the one at 1.48 V in 0.1 M KOH reported by Lee et al. [19], as we discussed before. The generated current density of IR-550 at 1.7 V vs RHE is about 9.2 mA cm⁻², which is slightly higher than the results of 8.5 mA cm⁻² reported by Lee et al., due to our slightly higher loading of IrO₂ (0.06 vs 0.05 mg-IrO₂ cm⁻²).

Compared to the Ir-550 sample, BTO-950AIR nanoparticles have a very low catalytic activity as evidenced by the high overpotential and low current density during both the ORR and the OER. In particular, the onset potential of OER on BTO-950AIR nanoparticles is around 1.8 V. These ORR and OER results indicate that calcination in air didn’t produce any good electrochemical catalyst. The ORR and OER activities of BTO-1300AR that was heat-treated in Ar are very similar to that of BTO-950AIR, showing insignificant activity for these oxygen reactions. In contrast, the OER and ORR catalytic activities of the oxygen deficient h-BaTiO₃₋ₓ rich BTO-1300VAC nanoparticles are significantly increased compared to BTO-950AIR and BTO-1300AR samples. When further compared to Ir-550 samples, the large reduction of overpotential during the OER is observed with the BTO-1300VAC nanoparticles indicated by a negative shift of the determined onset potentials. The largely negative shift of onset potential of OER on BTO-1300VAC (1.3 V) suggests the nature of active sites on BTO-1300VAC is more intrinsically active than those on IrO₂ (1.5 V). Furthermore, the mass activity of BTO-1300VAC and Ir-550 samples was compared in Figure 6b, as a function of potentials during the OER. The BTO-1300VAC sample generates larger current density than state-of-the-art IrO₂ catalysts (Ir-550) at relatively low potential (<1.6 V). However, the measured current density for Ir-550 at high potentials (>1.6 V) rapidly increases and exceeds that for BTO-1300VAC. Compared to traditional perovskite oxides, IrO₂ has much higher electrical conductivity. In addition, although the detailed active sites structures on the oxygen-deficient BaTiO₃₋ₓ remain unknown, active site density of perovskite is likely much higher than that of IrO₂. Thus, the low current density measured with the BTO-1300VAC at higher potentials is mainly due to the insufficient electron conductivity and number of active sites, relative to the IrO₂ catalyst. Tuning the synthesis conditions to further increase the fraction of oxygen-deficient h-BaTiO₃₋ₓ is ongoing in our research in order to improve the current densities at high potential range for the OER. It is worth noting that BTO-
1300VAC sample has a distinct hysteresis loop during the measurement of N₂ adsorption/desorption at 77 K with an average pore size of 12.8 nm, both suggesting a mesoporous feature in the catalyst. The BET specific surface area of BTO-1300VAC is calculated to be 24.7 $\text{m}^2\text{g}^{-1}$ that is comparable to that of IrO₂ ($21.1 \text{m}^2\text{g}^{-1}$). Usually, surface areas of oxide catalysts (i.e. BaTiO₃ and IrO₂) are much lower than those of traditional carbon black-based Fe-N-C catalysts (a few hundred $\text{m}^2\text{g}^{-1}$) [44].

On the other hand, during the ORR, BTO-1300VAC also exhibited much enhanced activity (still lower than state-of-the-art Pt catalysts in alkaline electrolyte) [45-47], relative to BTO-950AIR, BTO-1300AR, and Ir-550 nanoparticles, evidenced by the more positive onset and half-wave potentials. Furthermore, the different behavior observed with BTO-1300AR and BTO-1300VAC during the ORR and OER reveals that their natures of active sites are not identical and more intrinsically active ORR sites were derived from oxygen-deficiency on h-BaTiO₃ perovskite as an efficient bifunctional oxygen electrocatalyst.

**Figure 6** (a) Steady-state polarization plots of the ORR and OER for Ir-550, BTO-950AIR, BTO-1300AR, and BTO-1300VAC samples in 0.1 M NaOH electrolyte at 25 °C and 900 rpm, (b) comparison of mass activity between BTO-1300VAC and Ir-550 catalysts during the OER, (c) and (d) steady-state ORR polarization plots and peroxide yield, respectively, of BaTiO₃ as a function of rotating speeds ranging from 400 to 2500 rpm, (e) Koutecky-Levich plots for the ORR on BTO-1300VAC catalyst RDE at 25 °C, (f) stability tests for the OER and ORR at constant potentials of 1.5 V and 0.6 V, respectively.
transfer \[14\]. Four-electron selectivity of the oxygen-deficient BTO-1300VAC during the ORR was further determined by calculating the peroxide yield as a function of rotating speeds. The peroxide yield was around 15% with a slight variation depending on rotating speeds. Generally, oxide catalysts suffer from high peroxide yield during the ORR (up to 45%) \[48\]. The much mitigated peroxide yield measured with the BTO-1300VAC samples further validates the high catalytic activity of oxygen-deficient perovskite catalysts for the ORR. Additionally, according to a modified Koutecky-Levich equation \[49\], the current densities (\(I/J\)) of the ORR generated at various potentials were plotted as a function of rotation speed (\(\omega^{-1/2}\)) showing a linear relationship (Figure 6e). Thus, by calculating the slopes of Koutecky-Levich plots, an \(n\) value of 3.2-3.5 was obtained for BTO-1300VAC catalyst in the potential range from 0.40 V to 0.50 V. It indicates that in alkaline aqueous media, the catalyst is able to electrocatalytically reduce \(O_2\) to \(OH^-\) nearly through a direct four-electron or two+two routes in both the limiting diffusion and the mixed kinetic-diffusion control regions.

The stability of the oxygen-deficient BaTiO$_{3-x}$-rich catalyst towards the OER and ORR at constant potentials 1.5 V and 0.6 V, respectively, was further studied and shown in Figure 6f. While initial decline was observed during the OER, steady current density was achieved after around 3000 s. Meanwhile, durable catalytic activity during the ORR on the oxygen-deficient BTO-1300VAC BaTiO$_{3-x}$ catalysts was obtained generating a constant current density of 1.6 mA cm$^{-2}$ at 0.6 V, which is in good agreement with the polarization plots shown in Figure 6a.

It is worth mentioning that the high-surface area Fe-N-C catalysts derived from carbon-nitrogen and iron precursors (e.g., polyaniline, melamine, dicyandiamide) through a high-temperature approach represents the state of the art of nonprecious metal catalysts for the ORR in terms of their high activity and reasonably good stability at low potential \[2,4,44,50\]. However, the poor durability at high potentials (>0.6 V) is a grand challenge of the Fe-N-C catalysts hindering their practical applications \[51,52\]. More importantly, the carbon-based Fe-N-C catalysts is not suitable for the more challenged OER at high potential due to their poor activity and stability resulting from dominant carbon oxidation \[24,25\]. Thanks to the intrinsic stability of oxides \[53\], the ORR and OER active bifunctional oxygen-deficient perovskite oxide catalysts are superior to the Fe-N-C catalysts in reversible electrochemical technologies (e.g., reversible fuel cells, metal-air batteries, and electrolyzers) with much feasible activity and stability \[1,3\].

**Conclusions**

In summary, in this work, a new type of oxygen-deficient BaTiO$_{3-x}$-rich perovskite catalyst was prepared through sol-gel method followed by high-temperature treatments under vacuum conditions. The prepared oxide particles are found to be nanosized with an average size of 110 nm. It was found that the phase structures and oxygen content of the BaTiO$_3$ depend greatly on the heating temperatures and type of atmosphere. While the air calcined sample contains single phase \(t\)-BaTiO$_3$, the argon calcined sample consists of \(t\)-BaTiO$_3$, TiC and BaCO$_3$. Both of these two samples show very low electrochemical activity for both the oxygen reduction and oxygen evolution reactions, suggesting that \(\tau\)-BaTiO$_3$, TiC, and BaCO$_3$ are not active catalyst for oxygen electrocatalysis. Importantly, neutron analysis indicated an oxygen-deficient hexagonal BaTiO$_{2.76}$ crystal structure can be generated by preparing BaTiO$_3$ at 1300 °C under vacuum conditions. The oxygen-deficient hexagonal BaTiO$_{3-x}$-rich catalyst exhibited excellent catalytic activity simultaneously for the ORR and OER in alkaline media. Especially, its OER activity exceeds state-of-the-art IrO$_2$ catalyst at relatively low potential (<1.6 V), evidenced by much more negative onset potentials and higher current densities. The exceptionally improved catalytic activities simultaneously for both oxygen reactions is likely due to the oxygen vacancies in \(\tau\)-BaTiO$_3$ crystal structures, facilitating reactants adsorption and charge transfer. This work has demonstrated a new type of bifunctional nonprecious metal catalyst through creating oxygen deficiency on a perovskite for oxygen reduction and evolution, holding great promise to be applied in reversible electrochemical energy conversion and storage technologies such as metal-air batteries and regener-ated fuel cells. A more detailed understanding of the mechanism for oxygen-deficient BaTiO$_{3-x}$ can be further obtained by using theoretical computation and simulation, which is one of our future focuses.

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**References**

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Oxygen-deficient BaTiO₃ – x perovskite as an efficient bifunctional oxygen electrocatalyst

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