La_{0.6}Sr_{1.4}MnO_{4+\delta} Layered Perovskite Oxide: Enhanced catalytic Activity for the Oxygen Reduction Reaction

Yarong Wang
Zhibin Yang
Fanliang Liu
Chao Jin
Jiao Wu

See next page for additional authors

Follow this and additional works at: http://scholarcommons.sc.edu/emec_facpub

Part of the Applied Mechanics Commons, Electro-Mechanical Systems Commons, and the Energy Systems Commons

Publication Info
Published in RSC Advances, Volume 51, Issue 2, 2015, pages 974-980.
©RSC Advances 2015, Royal Society of Chemistry.
This article cannot be redistributed or further made available.
This article was first published by the Royal Society of Chemistry and can be found at http://dx.doi.org/10.1039/C4RA11588K
http://dx.doi.org/10.1039/C4RA11588K

This Article is brought to you for free and open access by the Mechanical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact SCHOLARC@mailbox.sc.edu.
Author(s)
Yarong Wang, Zhibin Yang, Fanliang Liu, Chao Jin, Jiao Wu, Ming Shen, Ruizhi Yang, and Fanglin Chen

This article is available at Scholar Commons: http://scholarcommons.sc.edu/emec_facpub/267
Carbon-coating functionalized La$_{0.6}$Sr$_{1.4}$MnO$_{4+\delta}$ layered perovskite oxide: enhanced catalytic activity for the oxygen reduction reaction

Yarong Wang,$^a$ Zhibin Yang,$^a$ Fanliang Lu,$^a$ Chao Jin,$^a$† Jiao Wu,$^a$ Ming Shen,$^c$ Ruizhi Yang*,$^a$ and Fanglin Chen*$^d$

Efficient electrocatalysts for the oxygen reduction reaction (ORR) is a critical factor to influence the performance of lithium–oxygen batteries. In this study, La$_{0.6}$Sr$_{1.4}$MnO$_{4+\delta}$ layered perovskite oxide as a highly active electrocatalyst for the ORR has been prepared, and a carbon-coating layer with thickness <5 nm has been successfully introduced to enhance the electronic conductivity of the as-prepared oxide. XRD, XPS, Raman, SEM and TEM measurements were carried out to characterize the crystalline structure and morphology of these samples. Rotating ring-disk electrode (RRDE) technique has been used to study catalytic activities of the as-prepared catalysts for the ORR in 0.1 M KOH media. RRDE results reveal that carbon-coated La$_{0.6}$Sr$_{1.4}$MnO$_{4+\delta}$ exhibits better catalytic activity for the ORR. For the carbon-coated La$_{0.6}$Sr$_{1.4}$MnO$_{4+\delta}$, the ORR proceeds predominately via a direct four electron process, and a maximum cathodic current density of 6.70 mA cm$^{-2}$ at 2500 rpm has been obtained, which is close to that of commercial Pt/C electrocatalyst under the same testing conditions.

1. Introduction

In recent years, rechargeable lithium–oxygen batteries have been attracting more and more attention due to higher theoretical energy densities (5200 Wh kg$^{-1}$, including oxygen) than state-of-the-art lithium ion batteries. The lithium–oxygen battery will enable electric vehicles with driving ranges similar to those of gasoline-powered vehicles if successfully developed.\(^1\)\(^-\)\(^3\) Sluggish oxygen reduction reaction (ORR) at air electrode plays a vital role in the optimization of lithium–oxygen batteries. The exploration of efficient electrocatalysts for the ORR is highly necessary for the developing of the lithium–oxygen battery.\(^4\)\(^-\)\(^9\) Platinum-based materials have long been regarded as active and efficient catalysts for the ORR. However, the high price, limited storage, sluggish ORR process, and instability of platinum-based catalysts have greatly impeded the commercialization of metal–air batteries.\(^10\)\(^-\)\(^12\) Therefore, it is vital and urgent to explore highly efficient non-platinum catalysts for ORR in the air electrode. In recent years, mixed valence oxides of transition metals have attracted much attention because of their prominent advantages of abundance, low cost, environment-friendly, and considerable catalytic activity towards electrochemical ORR.

Among various types of metal oxides, perovskite oxides exhibit good cation ordering, which can provide disorder-free channels of oxygen vacancies to enhance the mobility of oxygen ions.\(^13\)\(^-\)\(^14\) Perovskite oxides have long been considered a promising material capable of catalyzing oxygen reduction in metal–air batteries with aqueous alkaline electrolytes.\(^15\)\(^-\)\(^19\) For example, La$_{0.6}$Ca$_{0.4}$CoO$_3$ perovskite oxide demonstrated promising performances as ORR catalyst for Zn–air battery in 9 M KOH solution.\(^15\) Over several years, some perovskite cathode materials of solid oxide fuel cells (SOFCs) have successively been reported as cathodic catalysts in lithium–oxygen batteries. Yang et al. prepared the Sr$_{0.95}$Ce$_{0.05}$CoO$_3$ perovskite catalysts loaded with copper nanoparticles and demonstrated improved round-trip efficiency in rechargeable Li–air batteries.\(^16\) Zhao et al. synthesized hierarchical mesoporous perovskite La$_{0.5}$Sr$_{0.5}$CoO$_{2.91}$ nanowires and used it as cathodic catalyst in lithium–oxygen batteries, which exhibited ultrahigh capacity over 11 000 mA h g$^{-1}$.\(^17\) As one of the most frequently-used cathode materials of SOFCs, La$_{0.8}$Sr$_{0.2}$MnO$_3$ perovskite oxide has also demonstrated promising catalytic properties in Li–air battery with non-aqueous electrolyte in many groups’ works.\(^18\)\(^-\)\(^19\) As mentioned above, the investigations into perovskite-type catalysts for lithium–oxygen batteries to date have mainly focused on ABO$_3$ cubic perovskite oxides, where A is main a rare earth metal and B is a transition metal.
In our previous reports, some “layered” perovskite oxides (A$_2$BO$_{4+d}$) with K$_2$NiF$_4$-type structure demonstrated higher oxygen ionic-transport properties and better electrocatalysis than that of traditional ABO$_3$ perovskite oxides, and we have successfully applied as electrode materials of SOFCs.\textsuperscript{20–22} A recent experimental study suggested that easily removable oxygen in doped La$_2$NiO$_4$ “layered” perovskite facilitated the reoxidation reaction of the transition metal, thereby leading to enhanced ORR activity.\textsuperscript{24} Unlike a simple perovskite, an A$_2$BO$_{4+d}$ layered perovskite can be described as stacked perovskite (ABO$_3$) layer alternating with rock-salt (AO) layers along the c direction (Fig. 1(a)). Because of the difference in A–O and B–O bond lengths, there is stress in the A$_2$BO$_{4+d}$ structure. Theoretically, it is an unstable structure. In order to eliminate this stress and maintain the structural stability, there are always interstitial oxygen between the ABO$_3$ perovskite layers and the AO rock-salt layers.\textsuperscript{20} In the A$_2$BO$_{4+d}$ materials, oxygen transport occurs via a complex mechanism combining interstitial migration in the rock-salt layers and vacancy migration in the perovskite planes, which endows A$_2$BO$_{4+d}$ materials of high oxygen ionic-transport properties and good electrocatalysis.\textsuperscript{22} However, electronic conductivity of A$_2$BO$_{4+d}$ layered perovskite is intrinsically poor because AO rock-salt layers could be considered to be an insulator, which limits its high-rate capability even if it could be used in lithium–oxygen batteries. Though doping of aliovalent cations onto A$_2$BO$_{4+d}$ could control lattice defect (B\textsuperscript{3+} and oxygen vacancy) and thus modify its electronic conductivity, this way cannot significantly improve electronic conductivity due to AO rock-salt layers.\textsuperscript{23} Surface coating with electronically conductive layers is an extraordinary effective way to enhance the electronic conductivity of A$_2$BO$_{4+d}$ material. Cu, Ag, carbon, and conducting polymers are currently utilized as electronic conducting coating materials.\textsuperscript{24,25} Among them, carbon coating is particularly attractive due to its high conductivity, electrochemical stability, low cost, and simplicity of implementation. In addition, intrinsic interconnection between carbon coating layers if also very effective to reduce the contact resistance between active material particles.\textsuperscript{26–28} On the other hand, the graphitic carbon coating layer need to be very thin (<5 nm) to allow easy and rapid penetration of oxygen ions. So, it is very challenging to develop an effective approach to produce ultrathin and uniform graphitic carbon coatings.

Herein, we report a bottom-up strategy to synthesize a carbon-coated La$_{0.6}$Sr$_{1.4}$MnO$_{4+d}$ composite (C-LSMO$_4$) through a pyrolysis and graphitization process. Sucrose was employed as carbon sources. Graphited carbon-coating was grown on the LSMO$_4$ surface through the realignment of carbon fragments aroused from the pyrolysis of sucrose. The carbon coating is compact and uniform along LSMO$_4$ surface. The electrochemical performance for the ORR of LSMO$_4$ perovskite oxide is remarkably improved with the assistance of carbon coating. To the best of our knowledge, we demonstrate for the first time that carbon-coated LSMO$_4$ catalysts exhibit excellent catalytic performance for the ORR.

2. Experimental section

2.1 Synthesis and preparation

All reagents were analytical grade chemicals and purchased from Guoyao Chemical Reagent Co. Ltd. La$_{0.6}$Sr$_{1.4}$MnO$_{4+d}$ (LSMO$_4$) powders were prepared through a citric acid–nitrate process as reported.\textsuperscript{23} First, La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$, and Mn(NO$_3$)$_2$ were mixed and dissolved in deionized water according to the stoichiometric compositions of LSMO$_4$; then a certain amount of citric acid was introduced, and the mole ratio of the total metal ion: citric acid was controlled around 1 : 1.5. NH$_4$OH was added to adjust the pH value to about 8.0. A brown gel was obtained after the solution was agitated over night at 80 °C. This gel was held at 250 °C for several hours to remove organics and form a powder precursor. Finally, the LSMO$_4$ powder was obtained after being calcined at 1000 °C for 8 h.

Preparation of the C-LSMO$_4$ sample was performed as follows: the obtained LSMO$_4$ powder was added into a certain amount of sucrose solution, the mass ratio was controlled at 8 : 1 between LSMO$_4$ and sucrose. The mixtures were heated with vigorous stirring till water was completely evaporated. The mixed powder was grinded and calcined at 900 °C for 12 h under Ar/H$_2$ (95 : 5 by volume ratio) atmosphere to get final C-LSMO$_4$. For comparisons, the as-prepared LSMO$_4$ powders without carbohydrate coatings were also reduced at 900 °C for 12 h under Ar/H$_2$ atmosphere. The sample was labeled as r-LSMO$_4$.

2.2 Characterization

The crystal phase of the as-prepared samples was characterized by X-ray powder diffraction (XRD, D/MAX-III-B-40KV, Japan, Cu K$_\alpha$ radiation; $\lambda = 0.15418$ nm). The morphologies and microstructures of the as-prepared samples were carried out using scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM; TecnaiG220) with an acceleration voltage of 200 kV. Raman spectroscopy was performed on a Jobin Yvon LabRAM HR800 instrument with a 514 nm excitation laser at a power of around 1 mW. X-ray photoelectron spectroscopy (XPS) analysis was performed with a hemispherical analyzer and using a monochromatized Al K$_\alpha$ (1486 eV) achromatic X-ray radiation. Nitrogen adsorption and desorption isotherms were measured at 77 K with BELSORPmini system (BEL Japan).
2.3 Electrochemical measurement

The procedures of electrode preparation and electrochemical tests were similar to our previous work.29–31 The electrochemical properties were evaluated with the rotating ring-disk electrode (RRDE) technique using a Fine Electrochemical system (AFMSRX rotator, and AFCBP1 bipotentiostat). The electrode layer was prepared on a glassy carbon (GC) disk by coating a layer of ultrasonically mixed C-LSMO4 and acetylene black ink with a C-LSMO4 loading of 0.4013 mg cm⁻². For comparison, samples of LSMO4 and r-LSMO4 were also be prepared and tested with the same procedure, respectively.

A conventional three-electrode electrochemical cell was used for all cyclic voltammetry (CV) and RRDE measurements. The ring electrode collection efficiency of this RRDE was measured to be 0.22. The ring potential was set at 0.5 V to induce complete peroxide decomposition as reported elsewhere.32 Before taking CV measurements, the KOH solution was bubbled with pure N₂ (99.99%) for at least 30 min to remove any dissolved O₂. For ORR measurements, the KOH solution was bubbled with pure O₂ (99.99%) over 30 min.

3. Results and discussion

3.1 Crystalline phase and microstructure characterization

Fig. 1(b) presents the XRD patterns of pristine LSMO4, reduced LSMO4 (r-LSMO4) and carbon-coated LSMO4 (C-LSMO4). Compared with the standard PDF card, all the diffraction peaks can be well indexed as K₂NiF₄ tetragonal structure with the space group I₄/mmm, except that a trace peak around 30° corresponding to La(OH)₃, and/or La₂O₃ for the pristine LSMO₄.33 The pattern peaks of r-LSMO4 and C-LSMO4 shifted gradually to the high angle direction corresponding to the lattice shrinkage, which roots in the loss of interstitial oxygen during the reducing process. Aguadero and co-authors reported that the lattice expansion phenomenon will happen if there is too much interstitial oxygen in layered perovskite oxide. Conversely, the lattice shrinkage will appear with the loss of interstitial oxygen.34 Because carbon coating layer could block the interstitial oxygen losing, to some degree, the shift difference of C-LSMO₄ is smaller than that of r-LSMO₄.

To further confirm XRD results, X-ray photoelectron spectroscopy (XPS) test was performed. As expected, the XPS survey spectrum given in Fig. 2(a) shows the La₃d, Sr₃d, Mn₂p, O₁s and C₁s peaks for the C-LSMO₄ sample. For comparison, Mn₂p spectra for pristine LSMO₄, r-LSMO₄ and C-LSMO₄ are also presented in Fig. 2(b)–(d), respectively. It can be seen that Mn–O binding energy increased with the difference of lattice shrinkage after reducing under Ar/H₂ atmosphere. This is consistent with the XRD results.

Raman microprobe spectroscopy was employed to character carbon coating layer. Raman spectra of r-LSMO₄, pure acetylene black after calcined at 900 °C for 12 h under Ar/H₂ atmosphere (named as pure C) and C-LSMO₄ are shown in Fig. 3, respectively. It can be clearly seen that there is no peaks for r-LSMO₄. While, the two intense broad bands at 1345 and 1570 cm⁻¹ for pure C and C-LSMO₄ are attributed to the D and G bands of carbon. The I_D/I_G ratio is associated with graphitization degree of various carbon materials, the smaller I_D/I_G ratio, the higher graphitization degree.34,35 The I_D/I_G value for the pure C is 0.94, while that for the C-LSMO₄ is 0.85, suggesting a relatively high graphitization degree of carbon-coating layer on the LSMO₄ surface.

Fig. 4(a)–(c) display SEM images of pristine LSMO₄, r-LSMO₄ and C-LSMO₄, respectively. Clearly, the as-prepared LSMO₄ (see Fig. 4(a)) was well dispersed nanoparticles with the size of 100–200 nm, and the powder was porous, which has relative high specific surface area and is generally accepted microstructure for the ORR. As shown in Fig. 4(b), the r-LSMO₄ without the protection of sucrose shows serious agglomeration after calcined at 900 °C for 12 h under Ar/H₂ atmosphere. By comparison, the C-LSMO₄ particle (Fig. 4(c)) well maintained their original morphology and size. The phenomenon can be interpreted that carbon-coating layer cut off interconnection of LSMO₄ particles and suppressed their agglomeration during sintering. So, we can say that carbon-coating layer not only enhances the electronic conductivity of LSMO₄, but also keeps the particle size for short oxygen ion transport pathway.

Carbon morphology and distribution greatly affect the catalytic behavior of as-prepared C-LSMO₄ sample. This is because full carbon coverage facilitates electron transfer along...
3.2 ORR properties of C-LSMO4

Fig. 6(a) show cyclic voltammetry (CV) scanning results of the as-prepared C-LSMO4 catalyst in O2 or N2 saturated 0.1 M KOH solutions, respectively. The C-LSMO4 catalyst displayed an exceptional ORR catalytic activity with an onset potential of ca. −0.12 V (vs. Ag/AgCl) and one reduction peaks at ca. −0.30 V (vs. Ag/AgCl).

To better understand the electrocatalytic performance and to evaluate the oxygen reduction kinetic parameters of the C-LSMO4 catalyst during the ORR process, rotating-ring-disk-electrode (RRDE) technique was performed. The measurements were carried out in a cathodic sweep with 10 mV s⁻¹ at various rotation speeds (ω) from 400 to 2500 rpm. Fig. 6(b) shows both ring current density (i_r) and disk current density (i_d) of the as-prepared C-LSMO4 catalyst recorded in O2 saturated 0.1 M KOH solution. From i_d curves, it can be seen that the diffusion limiting current densities increased as rotation speed increase from 400 to 2500 rpm. High rotation speeds lead to faster oxygen flux to electrodes surface and consequently larger currents. The transferred electrons number and the formation of peroxide species (OH₂⁻) involved in the ORR are two important parameters to verify the ORR catalytic pathway of the catalyst. The RRDE experiment involves holding the disk at potential E_d, where the reaction O + n e⁻/R produces a cathodic current i_d; the ring is kept at a sufficiently positive potential E_r (0.5 V), so that any R reaching the ring is rapidly oxidized. The ring current, i_r, is related to the disk current, i_d, by a quantity N, the capture coefficient. So the transferred electron number (n) and the contents of peroxide HO2⁻ during the ORR could be calculated, according to the eqn (1) and (2), respectively, as follows:

\[
n = 4 \frac{i_d}{i_d + (i_r/N)}
\]

Fig. 4 SEM images of pristine LSMO4 (a), r-LSMO4 (b), and C-LSMO4 (c), respectively.

Fig. 5 TEM images of C-LSMO4 with different magnifications, 100 nm bar (a), 20 nm bar (b) and 5 nm bar (c), respectively.

Fig. 6 CV curves of the as-prepared C-LSMO4 catalyst on a GC electrode in N2 (black dotted curve) and O2 (red curve) saturated 0.1 M KOH solution at room temperature (a); disk (i_d) and ring (i_r) current densities collected on BCFN electrode for the ORR (b); electron transfer number (n) and peroxide HO2⁻ calculated with i_d and i_r (c); Koutecky–Levich plots (d).
Published on 26 November 2014. Downloaded by University of South Carolina Libraries on 04/03/2015 17:01:39.

\[ \text{HO}_2^- \% = 100 \times \frac{2i_d/N}{i_d + (i_k/N)} \]  

where \( n \) is the transferred electron number during the ORR process, \( i_d \) is the disk current, \( i_k \) is the ring current, and \( N \) is the capture coefficient (here, \( N = 0.22 \)).

Fig. 6(c) displays the transferred electron number and the contents of peroxide \( \text{HO}_2^- \) during the ORR at 2500 rpm. The \( n \) values are 3.8–4.0 and the measured \( \text{HO}_2^- \) yields are below 8.0% over the measured potential range, indicating a 4e\(^-\) pathway for the C-LSMO\(_4\) catalyst during the ORR process.

The Koutecky–Levich plot was used to further characterize the ORR mechanism. According to \( i_d \) curves shown in Fig. 6(b), the K–L plots were calculated and displayed in Fig. 6(d) respectively, by using the following equations:\(^5,\text{38}\)

\[
\frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{i_{dl}}
\]  

\[
i_k = nF Ak \text{Co}_2
\]  

\[
i_{dl} = 0.62nF \text{Co}_2D_{0.5}v^{-1/6}w^{1/2} = Bw^{1/2}
\]  

\[
\frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{i_{dl}} = \frac{1}{i_k} + B^{-1/2}
\]

where \( i_d, i_k \) and \( i_{dl} \) are the tested disk current density, kinetic current density, and film diffusion limiting current density, respectively. \( B \) is the so-called “\( B \)-factor”. Furthermore, \( n \) is the number of electrons in the ORR, \( F \) is the Faraday constant (96 500 C mol\(^{-1}\)), \( A \) is the area of the disk electrode (0.196 cm\(^2\)), \( \text{Co}_2 \) is the oxygen concentration in 0.1 M KOH (1.14 \times 10\(^{-6}\) mol cm\(^{-3}\)), \( D_0 \) is the oxygen diffusion coefficient in 0.1 M KOH (1.73 \times 10\(^{-5}\) cm\(^2\) s\(^{-1}\)), \( v \) is the kinematic viscosity of the 0.1 M KOH solution (0.01 cm\(^2\) s\(^{-1}\)), \( \omega \) is the electrode rotation rate (rpm), \( k \) is the rate constant for the ORR. There should be a linear relationship between \( i_d^{-1} \) and \( \omega^{-1/2} \), the intercept is equal to \( i_k^{-1} \), and the number of the electron transferred during the reaction could be calculated from the slope.\(^5,\text{29–34}\)

From Fig. 6(d), it can be seen that all fitting plots appear well linear and parallel relationship, implying the first-order dependence of the ORR kinetics on the C-LSMO\(_4\) catalyst surface. Each straight line intercept corresponds to the kinetic current \( i_k \). According to the slope of K–L plots, the “\( B \)-factor” was determined with a value of 0.146 mA cm\(^{-2}\) \( \omega^{-1/2} \), and the electron number was further calculated with a value of 3.86. The result was also indicated a 4e\(^-\) pathway for the C-LSMO\(_4\) catalyst during the ORR process.

### 3.3 Comparison of ORR catalytic activities

To better understand the electrocatalytic performance of the C-LSMO\(_4\) catalyst during the ORR process, the comparison between the ORR activities on LSMO\(_4\), r-LSMO\(_4\) and pure C as measured with the RRDE is shown in Fig. 7. The ORR activity on commercial Pt/C (20 wt% Pt on carbon) is also included for comparison. The disk and ring currents were measured at 2500 rpm and normalized by the geometric surface area. According to the results shown in Fig. 7, the onset potential, half-wave potential and diffusion limiting current density of these five catalysts were displayed in Table 1. The ORR activity increase as follows: C < LSMO\(_4\) < r-LSMO\(_4\) < C-LSMO\(_4\) < Pt/C, as evidenced by these three parameters shown in Table 1. The diffusion limiting current density of \(-6.70 \text{ mA cm}^{-2}\) for the C-LSMO\(_4\) was obtained, which is near to that of Pt/C (\(-7.14 \text{ mA cm}^{-2}\)), and a half-wave potential difference of about 137 mV exists between C-LSMO\(_4\) and Pt/C. Considering our tested diffusion limiting current density and half-wave potential of the Pt/C are in good agreement with the values of Pt/C (20 wt% Pt) reported elsewhere,\(^37,\text{38}\) we can conclude that C-LSMO\(_4\) is more active and comparable to the activity of Pt/C. Fig. 8 shows the transferred electron number of these catalysts. The electron transfer number of 3.85–4.0 for C-LSMO\(_4\) was more comparable to that of Pt/C catalyst.

Fig. 9 shows Tafel plots of these four samples. The kinetic currents were derived from the mass-transport correction using eqn [6] to construct the Tafel plots. It can be observed that the smallest Tafel slope of 62 mV dec\(^{-1}\) was obtained for the C-LSMO\(_4\) at low overpotentials, which is close to the theoretical value of 2.303RT/F (i.e., 59 mV dec\(^{-1}\) at 25°C), where \( R \) is the universal gas constant, \( F \) is the Faraday constant, and \( T \) is the absolute temperature. The lower Tafel slope indicates the high intrinsic catalytic activity of C-LSMO\(_4\).

Oxygen species were analyzed by XPS to interpret electrochemical performances of three LSMO\(_4\) catalysts. Fig. 10(a)–(c) display O1s XPS spectra of LSMO\(_4\), r-LSMO\(_4\) and C-LSMO\(_4\), respectively. The signal at BE = ca. 530 eV is attributed to lattice oxygen (\( \text{O}^{2-}\)) and the one at BE = ca. 531 eV to surface adsorbed oxygen species (such as \( \text{O}^\cdot \), \( \text{O}_2^\cdot \) or \( \text{O}_3^\cdot \)).\(^40,\text{41}\) The lattice oxygen includes bulk lattice oxygen and interstitial oxygen. Here, both of bulk lattice oxygen and interstitial oxygen are contained.

| Table 1 | Summary of the ORR Catalytic characteristics of pristine LSMO\(_4\), r-LSMO\(_4\), C-LSMO\(_4\), Pt/C and pure C |
| --- | --- | --- |
| Catalyst | Onset potential (V vs. Ag/AgCl) | Half-wave potential (V vs. Ag/AgCl) | \( i_d \) (mA cm\(^{-2}\)) |
| LSMO\(_4\) | -0.240 | -0.383 | -4.28 |
| r-LSMO\(_4\) | -0.172 | -0.323 | -5.72 |
| LSMO\(_4\) | -0.149 | -0.306 | -6.70 |
| Pt/C | 0.003 | -0.169 | -7.14 |
| Pure C | -0.284 | -0.401 | -1.82 |
in A2BO4+ layered perovskite oxides, and the interstitial oxygen is preferentially to be lost during the reducing process. Furthermore, the lattice oxygen is more active than the surface oxygen. Therefore, the over interstitial oxygen will transfer to adsorbed oxygen during the reducing process of LSMO4.

Fig. 10(d) shows relative contents of different oxygen species in these three samples. According to the order of LSMO4, C-LSMO4 and r-LSMO4, it can be concluded that the content of lattice oxygen reduced, while that of adsorbed oxygen species increased. In alkaline media, several factors would be concerned for the ORR, such as O2 adsorption, HO2- decomposition, as well as ionic and electronic transportation.27 After reduced by Ar/H2 at high temperature, lattice oxygen number decreased, and there would contain more defects, which are beneficial to surface adsorption of O2 and dissociation of O–O bonds. As a result, reducing treated LSMO4 (r-LSMO4 and C-LSMO4) should exhibit better catalytic performance than that of pristine LSMO4. As for the comparison between r-LSMO4 and C-LSMO4, there are two other rationalized reasons which determine better catalytic performance of C-LSMO4. First, electrical conductivity plays an important role in affecting the catalytic activity of perovskite oxide. Carbon coating enhances the electrical conductivity by one or two orders of magnitude, which should greatly favor fast electronic transfer and reduce electrode polarization during the catalytic ORR process; second, C-LSMO4 is more porous and has higher surface area than r-LSMO4 as shown in Fig. 4(b) and (c). Higher surface areas permit more active sites for the contact between catalyst and electrolyte. More porous microstructure might facilitate the diffusion, adsorption, and transport of O2 gas. Therefore, the superiority of C-LSMO4 is understandable.

4. Conclusions

In conclusion, La0.6Sr1.4MnO4+ layered perovskite oxide has been synthesized and introduced as catalyst for oxygen reduction reaction. To enhance electronic conductivity of La0.6Sr1.4MnO4+ oxide, a surface carbon coating with thickness of <5.0 nm has successfully prepared. Carbon-coating layer not only enhances the electronic conductivity of the material, but also keeps the particle size for short distance of oxygen ion transport. Electrochemical investigations reveal that La0.6Sr1.4MnO4+ with carbon coating showed high activities for the ORR in alkaline media, which is comparable to those of commercial Pt/C catalyst.

Acknowledgements

The project was supported by National Natural Science Foundation of China (51272167, 21206101), Natural Science Foundation of Jiangsu Province, China (BK20141199), Natural Science Foundation of the Higher Education Institutions of Jiangsu Province, China (12KJB430010, 14KJB480005). F. Chen acknowledges the financial support from the HeteroFoAM Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001061.

Notes and references

29 A. Aguadero, M. Pérez and L. Daza, J. Power Sources, 2005, 151, 52.